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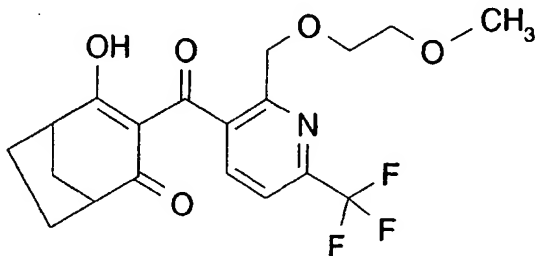
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(54) Title: HERBICIDAL COMPOSITION



(I)

(57) Abstract: Herbicidal composition which,
in addition to comprising customary inert
formulation adjuvants, comprises a) a compound
of formula (I) or an agronomically tolerable
salt of that compound, and b) a synergistically
effective amount of one or more compounds
of formulae 2.1 to 2.7 and the compounds
prosulfocarb, picolinafen, pyraflufen-ethyl, be-
flubutamid, fenoxaprop-P-ethyl, diclofop-methyl,
amidosulfuron, fluprimsulfuron, fluprimsul-
furon-methyl-sodium, metsulfuron-methyl,

sulfosulfuron, tribenuron-methyl, imazamethabenz-methyl, flucarbazone, chlorotoluron, isoproturon, methabenzthiazuron, bifenox,
fluoroglycofen-ethyl, imazosulfuron, diflufenican, bilanafos, ethalfluralin, trifluralin, fluthiamid, isoxaben, triallate, 2,4-DB,
dichlorprop, MCPA, MCPB, mecoprop, MCPP, mecoprop-P, clopyralid, fluroxypyr, quinmerac, benazolin-ethyl, difenzoquat,
cyhalofop-butyl, dithiopyr, quinclorac, prodiamine, benefin and trifluralin. The compositions according to the invention may also
comprise a safener. Compositions and methods for their use as herbicides, comprising a compound fo formula (I) and a safener are
also claimed.

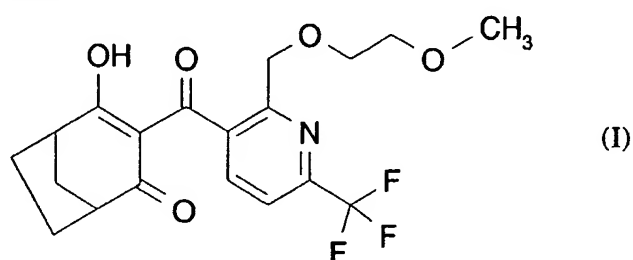


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Herbicidal composition

The present invention relates to a novel herbicidal composition comprising a herbicidal active ingredient combination that is suitable for selective weed control in crops of useful plants, for example in crops of maize. The invention relates also to a method of controlling weeds in crops of useful plants and to the use of the novel composition for that purpose.

The compound of formula I

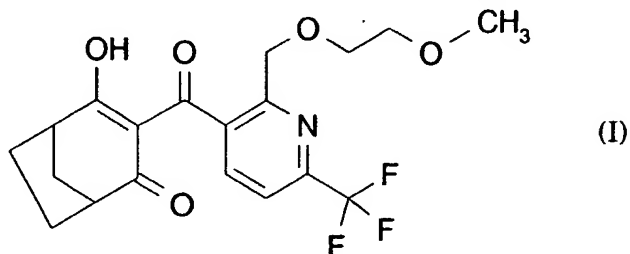


has herbicidal activity. The compound of formula I and its preparation are known, for example, from WO 01/94339.

Surprisingly, it has now been found that a combination of variable amounts of active ingredients, that is to say a combination of a compound of formula I with one or more of the known active ingredients listed below, some of which are also available commercially, develops a synergistic action that is capable of controlling, both pre-emergence and post-emergence, the majority of the weeds occurring especially in crops of useful plants.

There is therefore proposed according to the present invention a novel synergistic composition for selective weed control which, in addition to comprising customary inert formulation adjuvants, comprises as active ingredient a mixture of

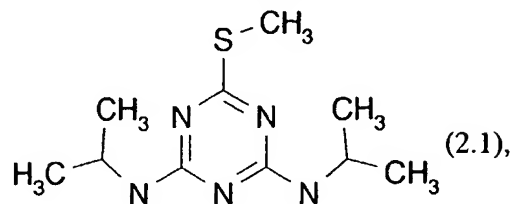
a) a herbicidally effective amount of the compound of formula I



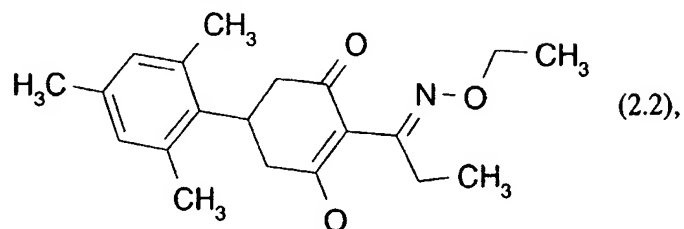
or of an agronomically tolerable salt of that compound, and

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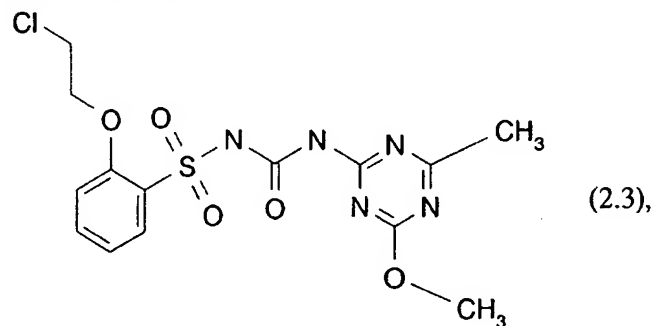
b) a synergistically effective amount of one or more compounds selected from the compound of formula 2.1



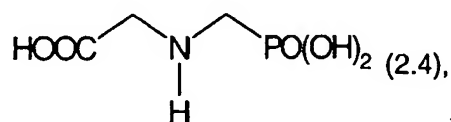
and the compound of formula 2.2



and the compound of formula 2.3

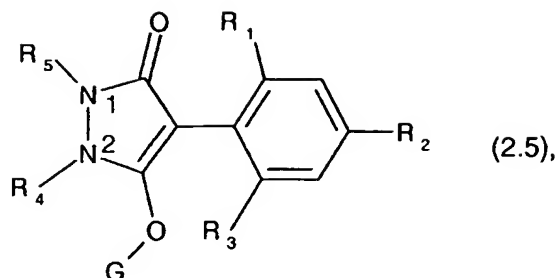


and the ammonium, isopropylammonium, sodium and trimesium salts of the compound of formula 2.4



and a compound of formula 2.5

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wherein

R_{01} , R_{02} and R_{03} are each independently of the others halogen, nitro, cyano, C_1 - C_4 alkyl, C_2 - C_4 alkenyl, C_2 - C_4 alkynyl, C_1 - C_4 haloalkyl, C_2 - C_6 haloalkenyl, C_3 - C_6 cycloalkyl, halo-substituted C_3 - C_6 cycloalkyl, C_1 - C_6 alkoxyalkyl, C_1 - C_6 alkylthioalkyl, hydroxy, mercapto, C_1 - C_6 alkoxy, C_3 - C_6 alkenyloxy, C_3 - C_6 alkynyloxy, C_1 - C_4 alkylcarbonyl, C_1 - C_4 alkoxycarbonyl, C_1 - C_4 alkylthio, C_1 - C_4 alkylsulfinyl, C_1 - C_4 alkylsulfonyl, amino, C_1 - C_4 alkylamino or di(C_1 - C_4 alkyl)-amino;

R_{04} and R_{05} together are a group

$-C-R_{06}(R_{07})-O-C-R_{08}(R_{09})-C-R_{010}(R_{011})-C-R_{012}(R_{013})-$ (Z_1),

$-C-R_{014}(R_{015})-C-R_{016}(R_{017})-O-C-R_{018}(R_{019})-C-R_{020}(R_{021})-$ (Z_2) or

$-C-R_{022}(R_{023})-C-R_{024}(R_{025})-C-R_{026}(R_{027})-O-C-R_{028}(R_{029})-$ (Z_3);

wherein R_{06} , R_{07} , R_{08} , R_{09} , R_{010} , R_{011} , R_{012} , R_{013} , R_{014} , R_{015} , R_{016} , R_{017} , R_{018} , R_{019} , R_{020} , R_{021} , R_{022} , R_{023} , R_{024} , R_{025} , R_{026} , R_{027} , R_{028} and R_{029} are each independently of the others hydrogen, halogen, C_1 - C_4 alkyl or C_1 - C_4 haloalkyl, wherein there may be either fused or spiro-bound to the carbon atoms of groups Z_1 , Z_2 or Z_3 an alkylene ring which together with the carbon atoms of groups Z_1 , Z_2 or Z_3 contains from 2 to 6 carbon atoms and which may be interrupted by oxygen, or that alkylene ring bridges at least one ring atom of the groups Z_1 , Z_2 or Z_3 ; G is hydrogen, $-C(X_1)-R_{030}$, $-C(X_2)-X_3-R_{031}$, $-C(X_4)-N(R_{032})-R_{033}$, $-SO_2-R_{034}$, an alkali metal, alkaline earth metal, sulfonium or ammonium cation, or $-P(X_5)(R_{035})-R_{036}$;

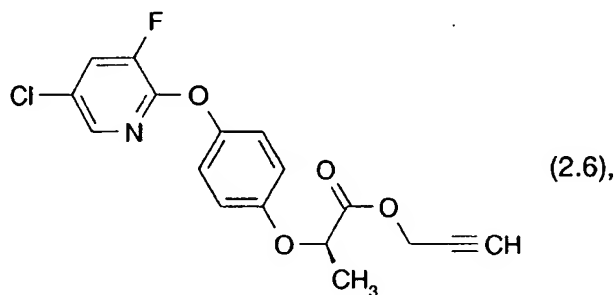
X_1 , X_2 , X_3 , X_4 and X_5 are each independently of the others oxygen or sulfur; and

R_{030} , R_{031} , R_{032} , R_{033} , R_{034} , R_{035} and R_{036} are each independently of the others hydrogen, C_1 - C_5 alkyl, C_1 - C_5 haloalkyl, C_2 - C_5 alkenyl, C_1 - C_5 alkoxyalkyl, C_3 - C_6 cycloalkyl or phenyl, and R_{034} may additionally be C_2 - C_{20} alkenyl, C_2 - C_{20} alkenyl substituted by halogen, alkylcarbonyl, alkoxycarbonyl, alkylcarbonyloxy, alkoxy, thioalkyl, alkylthiocarbonyl, alkylcarbonylthio, alkylsulfonyl, alkylsulfoxyl, alkylaminosulfonyl, dialkylaminosulfonyl, alkylsulfonyloxy, alkylsulfonylamino, alkylamino, dialkylamino, alkylcarbonylamino, dialkylcarbonylamino, alkyl-alkylcarbonylamino, cyano, (C_3 - C_7)cycloalkyl, (C_3 - C_7)heterocyclyl, trialkylsilyl, trialkylsilyloxy, phenyl, substituted phenyl, heteroaryl or by substituted heteroaryl, C_2 - C_{20} alkynyl, C_2 - C_{20}

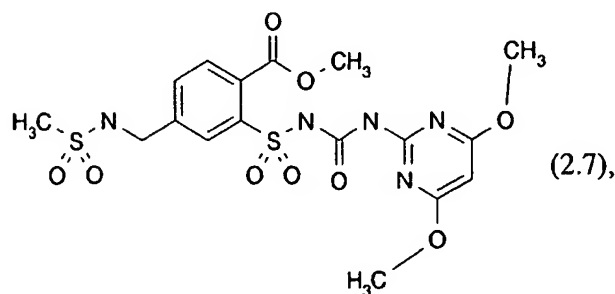
- 4 -

alkynyl substituted by halogen, alkylcarbonyl, alkoxycarbonyl, alkylcarbonyloxy, alkoxy, thioalkyl, alkylthiocarbonyl, alkylcarbonylthio, alkylsulfonyl, alkylsulfoxyl, alkylaminosulfonyl, dialkylaminosulfonyl, alkylsulfonyloxy, alkylsulfonylamino, alkylamino, dialkylamino, alkylcarbonylamino, dialkylcarbonylamino, alkyl-alkylcarbonylamino, cyano, (C₃-C₇)cycloalkyl, (C₃-C₇)heterocyclyl, trialkylsilyl, trialkylsilyloxy, phenyl, substituted phenyl, heteroaryl or by substituted heteroaryl, (C₁-C₇)cycloalkyl, (C₁-C₇)cycloalkyl substituted by halogen, haloalkyl, (C₁-C₆)alkyl, alkoxy, alkylcarbonyloxy, thioalkyl, alkylcarbonylthio, alkylamino, alkylcarbonylamino, trialkylsilyl or by trialkylsilyloxy, heteroaryl, heteroaryl substituted by halogen, haloalkyl, nitro, cyano, (C₁-C₆)alkyl, alkoxy, alkylcarbonyloxy, thioalkyl, alkylcarbonylthio, alkylamino, alkylcarbonylamino, trialkylsilyl or by trialkylsilyloxy, heteroaryloxy, substituted heteroaryloxy, heteroarylthio, substituted heteroarylthio, heteroarylamino, substituted heteroarylamino, diheteroarylamino, substituted diheteroarylamino, phenylamino, substituted phenylamino, diphenylamino, substituted diphenylamino, cycloalkylamino, substituted cycloalkylamino, dicycloalkylamino, substituted dicycloalkylamino, cycloalkoxy or substituted cycloalkoxy, as well as salts and diastereoisomers of the compounds of formula 2.5,

and the compound of formula 2.6



and the compound of formula 2.7



and the compounds prosulfocarb, picolinafen, pyraflufen-ethyl, beflubutamid, fenoxaprop-P-ethyl, diclofop-methyl, amidosulfuron, flupyrsulfuron, flupyrsulfuron-methyl-sodium, metsulfuron-methyl, sulfosulfuron, tribenuron-methyl, imazamethabenz-methyl, flucarbazone, chlorotoluron, isoproturon, methabenzthiazuron, bifenox, fluoroglycofen-ethyl, imazosulfuron, diflufenican, bilanafos, ethalfluralin, trifluralin, fluthiamid, isoxaben, triallate, 2,4-DB, dichlorprop, MCPA, MCPB, mecoprop, MCPP, mecoprop-P, clopyralid, fluroxypyr, quinmerac, benazolin-ethyl, difenzoquat, cyhalofop-butyl, dithiopyr, quinclorac, prodiamine, benefin and trifluralin.

The invention also includes the salts which the compound of formula I is able to form with amines, alkali metal and alkaline earth metal bases or quaternary ammonium bases. Of the alkali metal and alkaline earth metal hydroxides as salt-formers, special mention is to be made of the hydroxides of lithium, sodium, potassium, magnesium and calcium, but especially those of sodium and potassium.

Examples of amines suitable for ammonium salt formation are both ammonia and primary, secondary and tertiary C₁-C₁₈alkylamines, C₁-C₄hydroxyalkylamines and C₂-C₄alkoxyalkylamines, for example methylamine, ethylamine, n-propylamine, isopropylamine, the four isomers of butylamine, n-amylamine, isoamylamine, hexylamine, heptylamine, octylamine, nonylamine, decylamine, pentadecylamine, hexadecylamine, heptadecylamine, octadecylamine, methylethylamine, methylisopropylamine, methylhexylamine, methylnonylamine, methylpentadecylamine, methyloctadecylamine, ethylbutylamine, ethylheptylamine, ethyloctylamine, hexylheptylamine, hexyloctylamine, dimethylamine, diethylamine, di-n-propylamine, diisopropylamine, di-n-butylamine, di-n-amylamine, diisoamylamine, dihexylamine, diheptylamine, dioctylamine, ethanolamine, n-propanolamine, isopropanolamine, N,N-diethanolamine, N-ethylpropanolamine, N-butylethanolamine, allylamine, n-butenyl-2-amine, n-pentenyl-2-amine, 2,3-dimethylbutenyl-2-amine, dibutenyl-2-amine, n-hexenyl-2-amine, propylenediamine, trimethylamine, triethylamine, tri-n-propylamine, triisopropylamine, tri-n-butylamine, triisobutylamine, tri-sec-butylamine, tri-n-amylamine, methoxyethylamine and ethoxyethylamine; heterocyclic amines, for example pyridine, quinoline, isoquinoline, morpholine, piperidine, pyrrolidine, indoline, quinuclidine and azepine; primary arylamines, for example anilines, methoxyanilines, ethoxyanilines, o-, m- and p-toluidines, phenylenediamines, benzidines, naphthylamines and o-, m- and p-chloroanilines; but especially triethylamine, isopropylamine and diisopropylamine.

It is extremely surprising that the combination of the compound of formula I with one or more active ingredients selected from formulae 2.1 to 2.7 and the compounds prosulfocarb, picolinafen, pyraflufen-ethyl, beflubutamid, fenoxaprop-P-ethyl, diclofop-methyl, amidosulfuron, flupyrsulfuron, flupyrsulfuron-methyl-sodium, metsulfuron-methyl, sulfosulfuron, tribenuron-methyl, imazamethabenz-methyl, flucarbazone, chlorotoluron, isoproturon, methabenzthiazuron, bifenox, fluoroglycofen-ethyl, imazosulfuron, diflufenican, bilanafos, ethalfluralin, trifluralin, fluthiamid, isoxaben, triallate, 2,4-DB, dichlorprop, MCPA, MCPB, mecoprop, MCPP, mecoprop-P, clopyralid, fluroxypyr, quinmerac, benazolin-ethyl, difenzoquat, cyhalofop-butyl, dithiopyr, quinclorac, prodiamine, benefin and trifluralin exceeds the additive action on the weeds to be controlled that is to be expected in principle and thus broadens the range of action of the individual active ingredients especially in two respects: firstly, the rates of application of the individual compounds of formulae I and 2.1 to 2.7 and the compounds prosulfocarb, picolinafen, pyraflufen-ethyl, beflubutamid, fenoxaprop-P-ethyl, diclofop-methyl, amidosulfuron, flupyrsulfuron, flupyrsulfuron-methyl-sodium, metsulfuron-methyl, sulfosulfuron, tribenuron-methyl, imazamethabenz-methyl, flucarbazone, chlorotoluron, isoproturon, methabenzthiazuron, bifenox, fluoroglycofen-ethyl, imazosulfuron, diflufenican, bilanafos, ethalfluralin, trifluralin, fluthiamid, isoxaben, triallate, 2,4-DB, dichlorprop, MCPA, MCPB, mecoprop, MCPP, mecoprop-P, clopyralid, fluroxypyr, quinmerac, benazolin-ethyl, difenzoquat, cyhalofop-butyl, dithiopyr, quinclorac, prodiamine, benefin and trifluralin are reduced while a good level of action is maintained and, secondly, the composition according to the invention achieves a high level of weed control also in those cases where the individual substances, in the range of low rates of application, have become useless from the agronomic standpoint. The result is a considerable broadening of the spectrum of weeds and an additional increase in selectivity in respect of the crops of useful plants, as is necessary and desirable in the event of an unintentional overdose of active ingredient. The composition according to the invention, while retaining excellent control of weeds in crops of useful plants, also allows greater flexibility in succeeding crops.

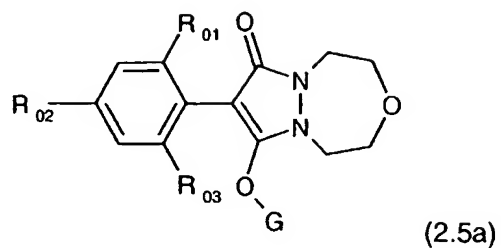
The composition according to the invention can be used against a large number of agronomically important weeds, such as *Stellaria*, *Nasturtium*, *Agrostis*, *Digitaria*, *Avena*, *Setaria*, *Sinapis*, *Lolium*, *Solanum*, *Phaseolus*, *Echinochloa*, *Scirpus*, *Monochoria*, *Sagittaria*, *Bromus*, *Alopecurus*, *Sorghum halepense*, *Rottboellia*, *Cyperus*, *Abutilon*, *Sida*, *Xanthium*, *Amaranthus*, *Chenopodium*, *Ipomoea*, *Chrysanthemum*, *Galium*, *Viola* and *Veronica*. The

composition according to the invention is suitable for all methods of application conventionally used in agriculture, for example pre-emergence application, post-emergence application and seed dressing. The composition according to the invention is suitable especially for controlling weeds in crops of useful plants, such as cereals, rape, sugar beet, sugar cane, plantation crops, rice, maize and soybeans, as well as for non-selective weed control.

"Crops" are to be understood to mean also those crops which have been made tolerant to herbicides or classes of herbicides (e.g. HPPD inhibitors, ALS inhibitors, EPSPS (5-enol-pyruvyl-shikimate-3-phosphate-synthase) inhibitors, GS (glutamine-synthetase) inhibitors). An example of crops that have been made tolerant to imidazolinones, for example imazamox, as a result of conventional methods of breeding (mutagenesis) is Clearfield® summer rape (Canola). Examples of crops that have been made tolerant to herbicides or classes of herbicides as a result of genetic engineering methods are glyphosate- or glufosinate-resistant maize varieties, which are commercially available under the trade names RoundupReady® and LibertyLink®.

Preferred synergistic mixtures according to the invention comprise as active ingredients a compound of formula I and a compound of formula 2.5a, as shown in Table 1:




Table 1: Compounds of formula 2.5a:



Comp. No.	R ₀₁	R ₀₂	R ₀₃	G	Phys. data
1.001	CH ₃	CH ₃	CH ₃	H	m.p. 245°C
1.002	CH ₃	CH ₃	CH ₃	C(O)C(CH ₃) ₃	m.p. 135-136°C
1.003	CH ₃	CH ₃	CH ₃	C(O)OCH ₂ CH ₃	
1.004	CH ₂ CH ₃	CH ₃	CH ₃	H	m.p. 182-185°C
1.005	CH ₂ CH ₃	CH ₃	CH ₃	C(O)C(CH ₃) ₃	m.p. 110-113°C
1.006	CH ₂ CH ₃	CH ₃	CH ₃	C(O)OCH ₂ CH ₃	
1.007	CH ₂ CH ₃	CH ₃	CH ₂ CH ₃	H	m.p. 189-191°C
1.008	CH ₂ CH ₃	CH ₃	CH ₂ CH ₃	C(O)C(CH ₃) ₃	m.p. 122-124°C
1.009	CH ₂ CH ₃	CH ₃	CH ₂ CH ₃	C(O)OCH ₂ CH ₃	m.p. 114-116°C
1.010	CH=CH ₂	CH ₃	CH ₃	H	m.p. 165-170°C
1.011	CH=CH ₂	CH ₃	CH ₃	C(O)C(CH ₃) ₃	m.p. 111-113°C
1.012	CH=CH ₂	CH ₃	CH ₂ CH ₃	H	
1.013	CH=CH ₂	CH ₃	CH=CH ₂	H	
1.014	CH=CH ₂	CH ₃	CH=CH ₂	C(O)C(CH ₃) ₃	

Comp. No.	R ₀₁	R ₀₂	R ₀₃	G	Phys. data
1.015	C≡CH	CH ₃	CH ₃	H	m.p. 179-184°C
1.016	C≡CH	CH ₃	CH ₃	C(O)C(CH ₃) ₃	m.p. 109-111°C
1.017	C≡CH	CH ₃	CH ₃	C(O)OCH ₂ CH ₃	
1.018	C≡CH	CH ₃	CH ₂ CH ₃	H	m.p. 189-193°C
1.019	C≡CH	CH ₃	CH ₂ CH ₃	C(O)C(CH ₃) ₃	
1.020	C≡CH	CH ₃	CH ₂ CH ₃	C(O)OCH ₂ CH ₃	
1.021	C≡CH	CH ₃	C≡CH	H	m.p. 300°C
1.022	C≡CH	CH ₃	C≡CH	C(O)C(CH ₃) ₃	m.p. 183-185°C
1.023	C≡CH	CH ₃	C≡CH	C(O)OCH ₂ CH ₃	
1.024	C≡CH	CH ₃	CH=CH ₂	H	
1.025	C≡CCH ₃	CH ₃	CH ₃	H	m.p. 179-181°C
1.026	C≡CCH ₃	CH ₃	CH ₃	C(O)C(CH ₃) ₃	m.p. 128-129°C
1.027	C≡CCH ₃	CH ₃	CH ₃	C(O)OCH ₂ CH ₃	
1.028	C≡CCH ₃	CH ₃	CH ₂ CH ₃	H	
1.029	C≡CCH ₃	CH ₃	CH ₂ CH ₃	C(O)C(CH ₃) ₃	
1.030	C≡CCH ₃	CH ₃	C≡CCH ₃	H	
1.031	C≡CCH ₃	CH ₃	C≡CCH ₃	C(O)C(CH ₃) ₃	
1.032	CH ₂ CH ₂ CH ₃	CH ₃	CH ₃	H	m.p. 136-138°C
1.033	CH ₂ CH ₂ CH ₃	CH ₃	CH ₃	C(O)C(CH ₃) ₃	m.p. 65-67°C
1.034	CH ₂ CH ₂ CH ₃	CH ₃	CH ₃	C(O)OCH ₂ CH ₃	
1.035	CH ₂ CH ₂ CH ₃	CH ₃	CH ₂ CH ₃	H	
1.036	CH ₂ CH ₂ CH ₃	CH ₃	CH ₂ CH ₂ CH ₃	H	
1.037	CH ₂ CH ₂ CH ₃	CH ₃	CH ₂ CH ₂ CH ₃	C(O)C(CH ₃) ₃	

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Comp. No.	R ₀₁	R ₀₂	R ₀₃	G	Phys. data
1.038	CH ₂ CH ₂ CH ₃	CH ₃	CH ₂ CH ₂ CH ₃	C(O)OCH ₂ CH ₃	
1.039	CH ₂ CH ₂ CH ₃	CH ₃	C≡CH	H	
1.040	CH(CH ₃) ₂	CH ₃	CH ₃	H	m.p. 214-216°C
1.041	CH(CH ₃) ₂	CH ₃	CH ₃	C(O)C(CH ₃) ₃	m.p. 148-151°C
1.042	CH(CH ₃) ₂	CH ₃	CH ₂ CH ₃	H	
1.043	CH(CH ₃) ₂	CH ₃	C≡CH	H	
1.044		CH ₃	CH ₃	H	
1.045		CH ₃	CH ₂ CH ₃	H	
1.046		CH ₃	C≡CH	H	
1.047	CH ₂ CH=CH ₂	CH ₃	CH ₃	H	
1.048	CH ₂ CH=CH ₂	CH ₃	CH ₂ CH ₃	H	
1.049	CH ₂ CH=CH ₂	CH ₃	C≡CH	H	
1.050	CH ₂ CH ₂ CH ₂ CH ₃	CH ₃	CH ₃	H	
1.051	CH ₂ CH ₂ CH ₂ CH ₃	CH ₃	CH ₂ CH ₃	H	
1.052	N(CH ₂ CH ₃) ₂	CH ₃	CH ₃	H	
1.053	N(CH ₂ CH ₃) ₂	CH ₃	CH ₂ CH ₃	H	
1.054	CH ₂ OH	CH ₃	CH ₃	H	
1.055	CH ₂ OCH ₃	CH ₃	CH ₃	H	
1.056	CH ₂ OC(CH ₃) ₃	CH ₃	CH ₃	H	
1.057	CH ₃	CH ₂ CH ₃	CH ₃	H	
1.058	CH ₂ CH ₃	CH ₂ CH ₃	CH ₃	H	
1.059	CH ₂ CH ₃	CH ₂ CH ₃	CH ₂ CH ₃	H	m.p. 185-187°C
1.060	CH ₂ CH ₃	CH ₂ CH ₃	CH ₂ CH ₃	C(O)C(CH ₃) ₃	m.p. 126-128°C
1.061	CH ₂ CH ₃	CH ₂ CH ₃	CH ₂ CH ₃	C(O)OCH ₂ CH ₃	m.p. 105-107°C

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Comp. No.	R ₀₁	R ₀₂	R ₀₃	G	Phys. data
1.062	CH=CH ₂	CH ₂ CH ₃	CH=CH ₂	H	
1.063	C≡CH	CH ₂ CH ₃	C≡CH	H	
1.064	CH ₃	CH=CH ₂	CH ₃	H	
1.065	CH ₂ CH ₃	CH=CH ₂	CH ₂ CH ₃	H	
1.066	CH ₂ CH ₃	CH=CH ₂	CH ₃	H	
1.067	CH ₂ CH ₃	CH=CH ₂	CH ₃	C(O)C(CH ₃) ₃	m.p. 108-110°C
1.068	C≡CH	CH=CH ₂	C≡CH	H	
1.069	CH ₃	C≡CH	CH ₃	H	
1.070	CH ₂ CH ₃	C≡CH	CH ₃	H	m.p. 240-243°C
1.071	CH ₂ CH ₃	C≡CH	CH ₃	C(O)C(CH ₃) ₃	m.p. 138-140°C
1.072	CH ₂ CH ₃	C≡CH	CH ₃	C(O)OCH ₂ CH ₃	
1.073	CH ₂ CH ₃	C≡CH	CH ₂ CH ₃	H	
1.074	CH ₂ CH ₃	C≡CH	C≡CH	H	
1.075	C≡CH	C≡CH	C≡CH	H	
1.076	CH ₃	CH ₂ CH=CH ₂	CH ₃	H	
1.077	CH ₃	CH ₂ CH=CH ₂	CH ₂ CH ₃	H	
1.078	CH ₃	CH ₃	Br	H	m.p. 234-237°C
1.079	CH ₃	CH ₃	Br	C(O)C(CH ₃) ₃	m.p. 76-78°C
1.080	CH ₃	CH ₃	Br	C(O)OCH ₂ CH ₃	
1.081	CH ₂ CH ₃	CH ₃	Br	H	
1.082	C≡CH	CH ₃	Br	H	
1.083	CH ₃	Br	CH ₃	H	m.p. 298-299°C
1.084	CH ₂ CH ₃	Br	CH ₃	H	m.p. 261-263°C

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Comp. No.	R ₀₁	R ₀₂	R ₀₃	G	Phys. data
1.085	CH ₂ CH ₃	Br	CH ₃	C(O)C(CH ₃) ₃	m.p. 127-130°C
1.086	CH ₂ CH ₃	Br	CH ₃	C(O)OCH ₂ CH ₃	
1.087	CH ₂ CH ₃	Br	CH ₂ CH ₃	H	m.p. 238-241°C
1.088	Br	CH ₃	Br	H	
1.089	Br	CH ₃	Br	C(O)C(CH ₃) ₃	solid
1.090	Br	CH ₃	Br	C(O)OCH ₂ CH ₃	
1.091	CH ₃	Br	Br	H	solid
1.092	CH ₂ CH ₃	Br	Br	H	
1.093	CH ₃	CH ₃	Cl	H	solid
1.094	CH ₂ CH ₃	CH ₃	Cl	H	
1.095	CH ₃	Cl	CH ₃	H	solid
1.096	CH ₂ CH ₃	Cl	CH ₃	H	
1.097	CH ₂ CH ₃	Cl	CH ₂ CH ₃	H	solid
1.098	CH ₂ CH ₃	F	CH ₂ CH ₃	H	
1.099	CH ₂ CH ₃	F	C≡CH	H	solid
1.100	CH ₂ CH ₃	F	OCH ₃	H	
1.101	Cl	CH ₃	Cl	H	solid
1.102	CH ₃	Cl	Cl	H	
1.103	CH ₂ CH ₃	Cl	Cl	H	solid
1.104	Br	CH ₃	Cl	H	
1.105	CH ₃	Br	Cl	H	solid
1.106	CH ₃	Cl	Br	H	
1.107	CH ₂ CH ₃	Br	Cl	H	solid
1.108	CH ₂ CH ₃	Cl	Br	H	
1.109	OCH ₃	CH ₃	CH ₃	H	m.p. 178-179°C
1.110	OCH ₃	CH ₃	CH ₂ CH ₃	H	
1.111	OCH ₃	CH ₃	CH ₂ CH ₃	C(O)C(CH ₃) ₃	m.p. 146-147°C
1.112	OCH ₃	CH ₃	CH ₂ CH ₃	C(O)OCH ₂ CH ₃	

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Comp. No.	R ₀₁	R ₀₂	R ₀₃	G	Phys. data
1.113	OCH ₃	CH ₃	CH ₂ CH ₂ CH ₃	H	
1.114	OCH ₃	CH ₃	C≡CH	H	
1.115	OCH ₃	CH ₃	Br	H	
1.116	OCH ₃	CH ₃	OCH ₃	H	
1.117	C(O)CH ₃	CH ₃	CH ₃	H	solid
1.118	C(O)CH ₃	CH ₃	CH ₂ CH ₃	H	
1.119	CH ₃	C(O)CH ₃	CH ₂ CH ₃	C(O)C(CH ₃) ₃	m.p. 163-165°C
1.120	CH ₃	CH ₂ OH	CH ₂ CH ₃	H	
1.121	CH ₃	CH ₃	CH ₃	SO ₂ CH ₂ CHCH ₂	
1.122	CH ₃	CH ₃	CH ₃	SO ₂ CH ₂ CHCHCl	
1.123	CH ₃	CH ₃	CH ₃	SO ₂ CH ₂ CHCHCH ₃	
1.124	CH ₂ CH ₃	CH ₃	CH ₂ CH ₃	SO ₂ CH ₂ CHCH ₂	
1.125	CH ₂ CH ₃	CH ₃	CH ₂ CH ₃	SO ₂ CH ₂ CHCHCl	
1.126	CH ₂ CH ₃	CH ₃	CH ₂ CH ₃	SO ₂ CH ₂ CHCHCH ₃	

The compound of formula 2.7 is known by the name mesosulfuron and is described, for example, under Chemical Abstracts Registry Number 208465-21-8. Dichlorprop is described under Chemical Abstracts Registry Number 15165-67-0. The compounds of formula 2.5 are described, for example, in WO 01/17352 .

The following compounds of the composition according to the invention are described in The Pesticide Manual, eleventh ed., British Crop Protection Council, 1997:

Compound of formula and/or name	Pesticide Manual eleventh ed., Entry No.:
2.1 (Prometryn)	597
2.2 (Tralkoxydim)	717
2.3 (Triasulfuron)	723
2.4 (Glyphosate salts)	383
2.6 (Clodinafop-propargyl)	147
Prosulfocarb	612
Pyraflufen-ethyl	617

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Compound of formula and/or name	Pesticide Manual eleventh ed., Entry No.:
Fenoxaprop-P-ethyl	309
Diclofop-methyl	219
Amidosulfuron	21
Flupyr-sulfuron	348
Flupyr-sulfuron-methyl-sodium	348
Metsulfuron-methyl	498
Sulfosulfuron	668
Tribenuron-methyl	728
Imazamethabenz-methyl	411
Chlorotoluron	134
Isoproturon	433
Methabenzthiazuron	477
Bifenox	69
Fluoroglycofen-ethyl	344
Imazosulfuron	416
Diflufenican	232
Bilanafos	71
Ethalfuralin	279
Trifluralin	740
Fluthiamid	51
Isoxaben	435
Triallate	722
2,4-DB	199
MCPB	457
Clopyralid	153
Fluroxypyr	354
Quinmerac	636
Benazolin-ethyl	55
Difenzoquat	229
Dithiopyr	259
Quinclorac	635
Prodiamine	593
Benefin	57

The following compounds of the composition according to the invention are described in The Pesticide Manual, 12th ed., British Crop Protection Council, 2000:

Compound	Pesticide Manual 12th ed., Entry No.:
Picolinafen	621
Beflubutamid	57
Flucarbazone	357
Cyhalofop-butyl	191

The composition according to the invention comprises the compound of formula I and the active ingredients of formulae 2.1 to 2.7 and the compounds prosulfocarb, picolinafen, pyraflufen-ethyl, beflubutamid, fenoxaprop-P-ethyl, diclofop-methyl, amidosulfuron, flupyrsulfuron, flupyrsulfuron-methyl-sodium, metsulfuron-methyl, sulfosulfuron, tribenuron-methyl, imazamethabenz-methyl, flucarbazone, chlorotoluron, isoproturon, methabenzthiazuron, bifenox, fluoroglycofen-ethyl, imazosulfuron, diflufenican, bilanafos, ethalfluralin, trifluralin, fluthiamid, isoxaben, triallate, 2,4-DB, dichlorprop, MCPA, MCPB, mecoprop, MCPP, mecoprop-P, clopyralid, fluroxypyr, quinmerac, benazolin-ethyl, difenzoquat, cyhalofop-butyl, dithiopyr, quinclorac, prodiamine, benefin and trifluralin in any desired mixing ratio, usually with an excess of one component over the other. Generally, the mixing ratios (ratios by weight) of the compound of formula I and the mixing partners of formulae 2.1 to 2.7 and prosulfocarb, picolinafen, pyraflufen-ethyl, beflubutamid, fenoxaprop-P-ethyl, diclofop-methyl, amidosulfuron, flupyrsulfuron, flupyrsulfuron-methyl-sodium, metsulfuron-methyl, sulfosulfuron, tribenuron-methyl, imazamethabenz-methyl, flucarbazone, chlorotoluron, isoproturon, methabenzthiazuron, bifenox, fluoroglycofen-ethyl, imazosulfuron, diflufenican, bilanafos, ethalfluralin, trifluralin, fluthiamid, isoxaben, triallate, 2,4-DB, dichlorprop, MCPA, MCPB, mecoprop, MCPP, mecoprop-P, clopyralid, fluroxypyr, quinmerac, benazolin-ethyl, difenzoquat, cyhalofop-butyl, dithiopyr, quinclorac, prodiamine, benefin and trifluralin are from 1:2000 to 2000:1, especially from 200:1 to 1:200.

The rate of application may vary within wide limits and depends on the nature of the soil, the method of application (pre- or post-emergence; seed dressing; application to the seed furrow; no tillage application etc.), the crop plant, the weed to be controlled, the prevailing climatic conditions, and other factors governed by the method of application, the time of

application and the target crop. The active ingredient mixture according to the invention can generally be applied at a rate of from 1 to 5000 g of active ingredient mixture/ha.

The mixtures of the compound of formula I with the compounds of formulae 2.1 to 2.7 and the compounds prosulfocarb, picolinafen, pyraflufen-ethyl, beflubutamid, fenoxaprop-P-ethyl, diclofop-methyl, amidosulfuron, flupyrsulfuron, flupyrsulfuron-methyl-sodium, metsulfuron-methyl, sulfosulfuron, tribenuron-methyl, imazamethabenz-methyl, flucarbazone, chlorotoluron, isoproturon, methabenzthiazuron, bifenox, fluoroglycofen-ethyl, imazosulfuron, diflufenican, bilanafos, ethalfluralin, trifluralin, fluthiamid, isoxaben, triallate, 2,4-DB, dichlorprop, MCPA, MCPB, mecoprop, MCPP, mecoprop-P, clopyralid, fluroxypyr, quinmerac, benazolin-ethyl, difenzoquat, cyhalofop-butyl, dithiopyr, quinclorac, prodiamine, benefin and trifluralin may be used in unmodified form, that is to say as obtained in synthesis. Preferably, however, they are formulated in customary manner, together with the adjuvants conventionally employed in formulation technology, such as solvents, solid carriers or surfactants, for example into emulsifiable concentrates, directly sprayable or dilutable solutions, dilute emulsions, wettable powders, soluble powders, dusts, granules or microcapsules. As with the nature of the compositions, the methods of application, such as spraying, atomising, dusting, wetting, scattering or pouring, are chosen in accordance with the intended objectives and the prevailing circumstances.

The formulations, that is to say the compositions, preparations or mixtures comprising the active ingredients of formulae I and 2.1 to 2.7 and the compounds prosulfocarb, picolinafen, pyraflufen-ethyl, beflubutamid, fenoxaprop-P-ethyl, diclofop-methyl, amidosulfuron, flupyrsulfuron, flupyrsulfuron-methyl-sodium, metsulfuron-methyl, sulfosulfuron, tribenuron-methyl, imazamethabenz-methyl, flucarbazone, chlorotoluron, isoproturon, methabenzthiazuron, bifenox, fluoroglycofen-ethyl, imazosulfuron, diflufenican, bilanafos, ethalfluralin, trifluralin, fluthiamid, isoxaben, triallate, 2,4-DB, dichlorprop, MCPA, MCPB, mecoprop, MCPP, mecoprop-P, clopyralid, fluroxypyr, quinmerac, benazolin-ethyl, difenzoquat, cyhalofop-butyl, dithiopyr, quinclorac, prodiamine, benefin and trifluralin and, optionally, one or more solid or liquid formulation adjuvants, are prepared in a manner known *per se*, e.g. by intimately mixing and/or grinding the active ingredients with the formulation adjuvants, for example solvents or solid carriers. Surface-active compounds (surfactants) may additionally also be used in the preparation of the formulations.

Examples of solvents and solid carriers are given, for example, on page 6 of WO 97/34485.

Depending on the nature of the compound of formula I to be formulated, suitable surface-active compounds are non-ionic, cationic and/or anionic surfactants and surfactant mixtures having good emulsifying, dispersing and wetting properties.

Examples of suitable anionic, non-ionic and cationic surfactants are listed, for example, on pages 7 and 8 of WO 97/34485.

Also suitable for the preparation of the herbicidal compositions according to the invention are the surfactants conventionally employed in formulation technology, which are described, *inter alia*, in "McCutcheon's Detergents and Emulsifiers Annual" MC Publishing Corp., Ridgewood New Jersey, 1981, Stache, H., "Tensid-Taschenbuch", Carl Hanser Verlag, Munich/Vienna, 1981 and M. and J. Ash, "Encyclopedia of Surfactants", Vol. I-III, Chemical Publishing Co., New York, 1980-81.

The compositions according to the invention may additionally comprise an additive containing an oil of vegetable or animal origin, a mineral oil, alkyl esters thereof, or mixtures of such oils and oil derivatives.

The amounts of oil additive used in the composition according to the invention are usually from 0.01 to 2 %, relative to the spray mixture. For example, the oil additive can be added to the spray tank once the spray mixture has been prepared in the desired concentration.

Preferred oil additives contain mineral oils or an oil of vegetable origin, for example rapeseed oil, olive oil or sunflower oil, emulsified vegetable oil, such as AMIGO®, which is obtainable from Rhône-Poulenc Canada Inc., alkyl esters of oils of vegetable origin, for example the methyl derivatives, or an oil of animal origin, such as fish oil or beef tallow. Special preference is given to "additive type A", which essentially comprises as the active components 80 % by weight of alkyl esters of fish oils and 15 % by weight of methylated rapeseed oil, as well as 5 % by weight of conventional emulsifiers and pH modifiers.

Especially preferred oil additives comprise alkyl esters of higher fatty acids (C₈-C₂₂), especially the methyl derivatives of C₁₂-C₁₈ fatty acids, for example the methyl esters of lauric

acid, palmitic acid and oleic acid. These esters are known as methyl laurate (CAS-111-82-0), methyl palmitate (CAS-112-39-0) and methyl oleate (CAS-112-62-9). A preferred fatty acid methyl ester derivative is Emery® 2230 and 2231 (Henkel subsidiary Cognis GMBH, DE)

The application and the action of the oil additives can be improved by combining them with surface-active substances, such as non-ionic, anionic or cationic surfactants. Examples of suitable anionic, non-ionic and cationic surfactants are listed on pages 7 and 8 of WO 97/34485.

Preferred surface-active substances are anionic surfactants of the dodecylbenzenesulfonate type, especially the calcium salts thereof, and also non-ionic surfactants of the fatty alcohol ethoxylate type. Special preference is given to ethoxylated C₁₂-C₂₂ fatty alcohols having a degree of ethoxylation of from 5 to 40. Examples of commercially available, preferred surfactants are the Genapol types (Clariant AG, Muttenz, Switzerland). The concentration of the surface-active substances, relative to the additive as a whole, is generally from 1 to 30 % by weight.

Surface-active substances which are also preferably used are silicone surfactants, especially polyalkyl-oxide-modified heptamethyltrisiloxanes, as are commercially available, for example, as Silwet L-77®, as well as perfluorinated surfactants.

Examples of oil additives consisting of mixtures of oils or mineral oils or derivatives thereof with surfactants are Edenor ME SU®, Turbocharge® (Zeneca Agro, Stoney Creek, Ontario, CA) or, especially, Actipron® (BP Oil UK Limited, GB).

The addition of an organic solvent to the oil additive/surfactant mixture may effect a further increase in the action. Examples of suitable solvents are Solvesso® (ESSO) or Aromatic Solvent® (Exxon Corporation) types.

The concentration of such solvents may be from 10 to 80 % by weight of the total weight.

Such oil additives, which are also described, for example, in US-A-4 834 908, are especially preferred for the composition according to the invention. A very especially preferred oil additive is known by the name MERGE®, can be obtained from BASF Corporation and is described in essence, for example, in col. 5 of US-A-4 834 908 as Example COC-1. A further

oil additive that is preferred according to the invention is SCORE® (Novartis Crop Protection Canada.)

In addition to the oil additives listed above, it is also possible to add to the spray mixture, for increasing the action of the compositions according to the invention, formulations of alkyl-pyrrolidones, as are marketed commercially as Agrimax®, for example. In order to increase the action it is also possible to use formulations of synthetic latices, for example polyacrylamide, polyvinyl compounds or poly-1-p-menthene, as are available on the market as, for example, Bond®, Courier® or Emerald®. Propionic-acid-containing solutions, for example Eurogkem Pen-e-trate®, can also be added to the spray mixture as agents increasing their action.

To compositions according to the invention that comprise compounds of formula 2.5 there are preferably added one or more of the above-mentioned oil additives, or of the above-mentioned formulations of alkylpyrrolidones, synthetic latices, or propionic-acid-containing solutions.

The herbicidal formulations usually comprise from 0.1 to 99 % by weight, especially from 0.1 to 95 % by weight, of active ingredient mixture comprising the compound of formula I together with the compounds of formulae 2.1 to 2.7 and the compounds prosulfocarb, picolinafen, pyraflufen-ethyl, beflubutamid, fenoxaprop-P-ethyl, diclofop-methyl, amidosulfuron, flupyrsulfuron, flupyrsulfuron-methyl-sodium, metsulfuron-methyl, sulfosulfuron, tribenuron-methyl, imazamethabenz-methyl, flucarbazone, chlorotoluron, isoproturon, methabenzthiazuron, bifenox, fluoroglycofen-ethyl, imazosulfuron, diflufenican, bilanafos, ethalfluralin, trifluralin, fluthiamid, isoxaben, triallate, 2,4-DB, dichlorprop, MCPA, MCPB, mecoprop, MCPP, mecoprop-P, clopyralid, fluroxypyr, quinmerac, benazolin-ethyl, difenzoquat, cyhalofop-butyl, dithiopyr, quinclorac, prodiamine, benefin and trifluralin, from 1 to 99.9 % by weight of a solid or liquid formulation adjuvant, and from 0 to 25 % by weight, especially from 0.1 to 25 % by weight, of a surfactant.

Whereas commercial products will preferably be formulated as concentrates, the end user will normally employ dilute formulations. The compositions may also comprise further additives, such as stabilisers, for example vegetable oils or epoxidised vegetable oils (epoxidised coconut oil, rapeseed oil or soybean oil), anti-foams, for example silicone oil,

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preservatives, viscosity regulators, binders, tackifiers, and also fertilisers or other active ingredients. Preferred formulations have especially the following compositions:

(% = percent by weight)

Emulsifiable concentrates:

active ingredient mixture: 1 to 90 %, preferably 5 to 20 %
 surfactant: 1 to 30 %, preferably 10 to 20 %
 liquid carrier: 5 to 94 %, preferably 70 to 85 %

Dusts:

active ingredient mixture: 0.1 to 10 %, preferably 0.1 to 5 %
 solid carrier: 99.9 to 90 %, preferably 99.9 to 99 %

Suspension concentrates:

active ingredient mixture: 5 to 75 %, preferably 10 to 50 %
 water: 94 to 24 %, preferably 88 to 30 %
 surfactant: 1 to 40 %, preferably 2 to 30 %

Wettable powders:

active ingredient mixture: 0.5 to 90 %, preferably 1 to 80 %
 surfactant: 0.5 to 20 %, preferably 1 to 15 %
 solid carrier: 5 to 95 %, preferably 15 to 90 %

Granules:

active ingredient mixture: 0.1 to 30 %, preferably 0.1 to 15 %
 solid carrier: 99.5 to 70 %, preferably 97 to 85 %

The following Examples further illustrate but do not limit the invention.

<u>F1. Emulsifiable concentrates</u>	a)	b)	c)	d)
active ingredient mixture	5 %	10 %	25 %	50 %
calcium dodecylbenzenesulfonate	6 %	8 %	6 %	8 %
castor oil polyglycol ether	4 %	-	4 %	4 %
(36 mol of ethylene oxide)				

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octylphenol polyglycol ether (7-8 mol of ethylene oxide)	-	4 %	-	2 %
cyclohexanone	-	-	10 %	20 %
arom. hydrocarbon mixture	85 %	78 %	55 %	16 %

C₉-C₁₂

Emulsions of any desired concentration can be obtained from such concentrates by dilution with water.

<u>F2. Solutions</u>	a)	b)	c)	d)
active ingredient mixture	5 %	10 %	50 %	90 %
1-methoxy-3-(3-methoxy- propoxy)-propane	-	20 %	20 %	-
polyethylene glycol MW 400	20 %	10 %	-	-
N-methyl-2-pyrrolidone	-	-	30 %	10 %
arom. hydrocarbon mixture	75 %	60 %	-	-

C₉-C₁₂

The solutions are suitable for use in the form of microdrops.

<u>F3. Wettable powders</u>	a)	b)	c)	d)
active ingredient mixture	5 %	25 %	50 %	80 %
sodium lignosulfonate	4 %	-	3 %	-
sodium lauryl sulfate	2 %	3 %	-	4 %
sodium diisobutyl-naphthalene- sulfonate	-	6 %	5 %	6 %
octylphenol polyglycol ether (7-8 mol of ethylene oxide)	-	1 %	2 %	-
highly dispersed silicic acid	1 %	3 %	5 %	10 %
kaolin	88 %	62 %	35 %	-

The active ingredient is mixed thoroughly with the adjuvants and the mixture is thoroughly ground in a suitable mill, affording wettable powders which can be diluted with water to give suspensions of any desired concentration.

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<u>F4. Coated granules</u>	a)	b)	c)
active ingredient mixture	0.1 %	5 %	15 %
highly dispersed silicic acid	0.9 %	2 %	2 %
inorganic carrier	99.0 %	93 %	83 %

(diameter 0.1 - 1 mm)

e.g. CaCO_3 or SiO_2

The active ingredient is dissolved in methylene chloride and applied to the carrier by spraying, and the solvent is then evaporated off *in vacuo*.

<u>F5. Coated granules</u>	a)	b)	c)
active ingredient mixture	0.1 %	5 %	15 %
polyethylene glycol MW 200	1.0 %	2 %	3 %
highly dispersed silicic acid	0.9 %	1 %	2 %
inorganic carrier	98.0 %	92 %	80 %

(diameter 0.1 - 1 mm)

e.g. CaCO_3 or SiO_2

The finely ground active ingredient is uniformly applied, in a mixer, to the carrier moistened with polyethylene glycol. Non-dusty coated granules are obtained in this manner.

<u>F6. Extruder granules</u>	a)	b)	c)	d)
active ingredient mixture	0.1 %	3 %	5 %	15 %
sodium lignosulfonate	1.5 %	2 %	3 %	4 %
carboxymethylcellulose	1.4 %	2 %	2 %	2 %
kaolin	97.0 %	93 %	90 %	79 %

The active ingredient is mixed and ground with the adjuvants, and the mixture is moistened with water. The mixture is extruded and then dried in a stream of air.

<u>F7. Dusts</u>	a)	b)	c)
active ingredient mixture	0.1 %	1 %	5 %
talcum	39.9 %	49 %	35 %
kaolin	60.0 %	50 %	60 %

Ready-to-use dusts are obtained by mixing the active ingredient with the carriers and grinding the mixture in a suitable mill.

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<u>F8. Suspension concentrates</u>	a)	b)	c)	d)
active ingredient mixture	3 %	10 %	25 %	50 %
ethylene glycol	5 %	5 %	5 %	5 %
nonylphenol polyglycol ether (15 mol of ethylene oxide)	-	1 %	2 %	-
sodium lignosulfonate	3 %	3 %	4 %	5 %
carboxymethylcellulose	1 %	1 %	1 %	1 %
37 % aqueous formaldehyde solution	0.2 %	0.2 %	0.2 %	0.2 %
silicone oil emulsion	0.8 %	0.8 %	0.8 %	0.8 %
water	87 %	79 %	62 %	38 %

The finely ground active ingredient is intimately mixed with the adjuvants, giving a suspension concentrate from which suspensions of any desired concentration can be obtained by dilution with water.

It is often more practical for the compound of formula I and the mixing partner or partners of formulae 2.1 to 2.7 and the compounds prosulfocarb, picolinafen, pyraflufen-ethyl, beflubutamid, fenoxaprop-P-ethyl, diclofop-methyl, amidosulfuron, flupyr-sulfuron, flupyr-sulfuron-methyl-sodium, metsulfuron-methyl, sulfosulfuron, tribenuron-methyl, imazamethabenz-methyl, flucarbazone, chlorotoluron, isoproturon, methabenzthiazuron, bifenoxy, fluoroglycofen-ethyl, imazosulfuron, diflufenican, bilanafos, ethalfluralin, trifluralin, fluthiamid, isoxaben, triallate, 2,4-DB, dichlorprop, MCPA, MCPB, mecoprop, MCPP, mecoprop-P, clopyralid, fluroxypyr, quinmerac, benazolin-ethyl, difenzoquat, cyhalofop-butyl, dithiopyr, quinclorac, prodiamine, benefin and trifluralin to be formulated separately and then to be brought together in the desired mixing ratio in the applicator in the form of a "tank mixture" in water shortly before application.

The compositions according to the invention may additionally also comprise growth regulators, for example trinexapac (744), chlormequat chloride (129), clofencet (148), cyclanilide (170), ethephon (281), flurprimidol (355), gibberellic acid (379), inabenfide (421), maleic hydrazide (449), mefluidide (463), mepiquat chloride (465), paclobutrazol (548), prohexadione-calcium (595), uniconazole (746) or thidiazuron (703). The compositions according to the invention may also comprise fungicides, for example azoxystrobin (43), epoxiconazole (48), benomyl (60), bromuconazole (89), bitertanol (77), carbendazim (107),

cyproconazole (189), cyprodinil (190), diclomezine (220), difenoconazole (228), diniconazole (247), epoxiconazole (48), ethirimol (284), etridiazole (294), fenarimol (300), fenbuconazole (302), fencpiclonil (311), fenpropidin (313), fenpropimorph (314), ferimzone (321), fludioxonil (334), fluquinconazole (349), flutolanil (360), flutriafol (361), imazalil (410), ipconazole (426), iprodione (428), isoprothiolane (432), kasugamycin (438), kresoxim-methyl (439), spiroxamine (441), mepronil (466), myclobutanil (505), nuarimol (528), pefurazoate (554), pencycuron (556), phthalide (576), probenazole (590), prochloraz (591), propiconazole (607), pyrazophos (619), pyroquilon (633), quinoxifen (638), quintozone (639), tebuconazole (678), tetraconazole (695), thiabendazole (701), thifluzamide (705), triadimefon (720), triadimenol (721), tricyclazole (734), tridemorph (736), triflumizole (738), triforine (742), triticonazole (745) or vinclozolin (751). The number given in brackets after each active ingredient refers to the entry number of the active ingredient in The Pesticide Manual, eleventh ed., British Crop Protection Council, 1997.

Biological Examples:

A synergistic effect exists whenever the action of the active ingredient combination of the compound of formula I and 2.1 to 2.7 and prosulfocarb, picolinafen, pyraflufen-ethyl, beflubutamid, fenoxaprop-P-ethyl, diclofop-methyl, amidosulfuron, flupyrsulfuron, flupyrsulfuron-methyl-sodium, metsulfuron-methyl, sulfosulfuron, tribenuron-methyl, imazamethabenz-methyl, flucarbazone, chlorotoluron, isoproturon, methabenzthiazuron, bifenox, fluoroglycofen-ethyl, imazosulfuron, diflufenican, bilanafos, ethalfluralin, trifluralin, fluthiamid, isoxaben, triallate, 2,4-DB, dichlorprop, MCPA, MCPB, mecoprop, MCPP, mecoprop-P, clopyralid, fluroxypyr, quinmerac, benazolin-ethyl, difenzoquat, cyhalofop-butyl, dithiopyr, quinclorac, prodiamine, benefin and trifluralin is greater than the sum of the actions of the active ingredients applied separately.

The herbicidal action to be expected We for a given combination of two herbicides can be calculated as follows (see COLBY, S.R., "Calculating synergistic and antagonistic response of herbicide combinations", Weeds 15, pages 20-22, 1967):

$$We = X + [Y \cdot (100 - X) / 100]$$

wherein:

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X = percentage herbicidal action on treatment with the compound of formula I at a rate of application of p kg per hectare, compared with the untreated control (= 0 %).

Y = percentage herbicidal action on treatment with a compound of formula 2.1 to 2.7 and prosulfocarb, picolinafen, pyraflufen-ethyl, beflubutamid, fenoxaprop-P-ethyl, diclofop-methyl, amidosulfuron, flupyrsulfuron, flupyrsulfuron-methyl-sodium, metsulfuron-methyl, sulfosulfuron, tribenuron-methyl, imazamethabenz-methyl, flucarbazone, chlorotoluron, isoproturon, methabenzthiazuron, bifenoxy, fluoroglycofen-ethyl, imazosulfuron, diflufenican, bilanafos, ethalfluralin, trifluralin, fluthiamid, isoxaben, triallate, 2,4-DB, dichlorprop, MCPA, MCPB, mecoprop, MCPP, mecoprop-P, clopyralid, fluroxypyr, quinmerac, benazolin-ethyl, difenzoquat, cyhalofop-butyl, dithiopyr, quinclorac, prodiamine, benefin and trifluralin at a rate of application of q kg per hectare, compared with the untreated control.

We = expected herbicidal action (percentage herbicidal action compared with the untreated control) following treatment with the compounds of formula I and 2.1 to 2.7 and prosulfocarb, picolinafen, pyraflufen-ethyl, beflubutamid, fenoxaprop-P-ethyl, diclofop-methyl, amidosulfuron, flupyrsulfuron, flupyrsulfuron-methyl-sodium, metsulfuron-methyl, sulfosulfuron, tribenuron-methyl, imazamethabenz-methyl, flucarbazone, chlorotoluron, isoproturon, methabenzthiazuron, bifenoxy, fluoroglycofen-ethyl, imazosulfuron, diflufenican, bilanafos, ethalfluralin, trifluralin, fluthiamid, isoxaben, triallate, 2,4-DB, dichlorprop, MCPA, MCPB, mecoprop, MCPP, mecoprop-P, clopyralid, fluroxypyr, quinmerac, benazolin-ethyl, difenzoquat, cyhalofop-butyl, dithiopyr, quinclorac, prodiamine, benefin and trifluralin at a rate of application of p + q kg of active ingredient per hectare.

When the action actually observed is greater than the value to be expected We, there is a synergistic effect.

The synergistic effect of the combinations of the compound of formula I with the compounds of formulae 2.1 to 2.7 and the compounds prosulfocarb, picolinafen, pyraflufen-ethyl, beflubutamid, fenoxaprop-P-ethyl, diclofop-methyl, amidosulfuron, flupyrsulfuron, flupyrsulfuron-methyl-sodium, metsulfuron-methyl, sulfosulfuron, tribenuron-methyl, imazamethabenz-methyl, flucarbazone, chlorotoluron, isoproturon, methabenzthiazuron, bifenoxy, fluoroglycofen-ethyl, imazosulfuron, diflufenican, bilanafos, ethalfluralin, trifluralin, fluthiamid, isoxaben, triallate, 2,4-DB, dichlorprop, MCPA, MCPB, mecoprop, MCPP,

mecoprop-P, clopyralid, fluroxypyr, quinmerac, benazolin-ethyl, difenzoquat, cyhalofop-butyl, dithiopyr, quinclorac, prodiamine, benefin and trifluralin is demonstrated in the following Examples.

Experiment description pre-emergence test:

Monocotyledonous and dicotyledonous test plants are sown in standard soil in plastics pots. Directly after sowing, the test compounds are applied by spraying in the form of an aqueous suspension (500 litres of water/ha). The rates of application depend on the optimum concentrations ascertained under field conditions and greenhouse conditions. The test plants are then grown on in a greenhouse under optimum conditions. The tests are evaluated after 36 days (% action, 100 % = plant has died, 0 % = no phytotoxic action). The mixtures used in this test exhibit good results.

Experiment description post-emergence test

The test plants are grown to the 2- to 3-leaf stage in plastics pots under greenhouse conditions. A standard soil is used as cultivation substrate. At the 2- to 3-leaf stage, the herbicides are applied to the test plants on their own and as a mixture. The test compounds are applied in the form of an aqueous suspension in 500 litres of water/ha. The rates of application depend on the optimum concentrations ascertained under field conditions and greenhouse conditions. The tests are evaluated after 33 days (% action, 100 % = plant has died, 0 % = no phytotoxic action). In this test too, the mixtures used exhibit good results.

It has been shown, surprisingly, that particular safeners are suitable for mixing with the synergistic composition according to the invention. The present invention accordingly relates also to a selectively herbicidal composition for controlling grasses and weeds in crops of useful plants, especially in crops of maize, which comprises a compound of formula I, one or more compounds selected from the compounds of formulae 2.1 to 2.7 and the compounds prosulfocarb, picolinafen, pyraflufen-ethyl, beflubutamid, fenoxaprop-P-ethyl, diclofop-methyl, amidosulfuron, flupyr-sulfuron, flupyr-sulfuron-methyl-sodium, metsulfuron-methyl, sulfosulfuron, tribenuron-methyl, imazamethabenz-methyl, flucarbazone, chlorotoluron, isoproturon, methabenzthiazuron, bifenox, fluoroglycofen-ethyl, imazosulfuron, diflufenican, bilanafos, ethalfluralin, trifluralin, fluthiamid, isoxaben, triallate, 2,4-DB, dichlorprop, MCPA, MCPB, mecoprop, MCPP, mecoprop-P, clopyralid, fluroxypyr, quinmerac, benazolin-ethyl, difenzoquat, cyhalofop-butyl, dithiopyr, quinclorac, prodiamine, benefin and trifluralin, and a

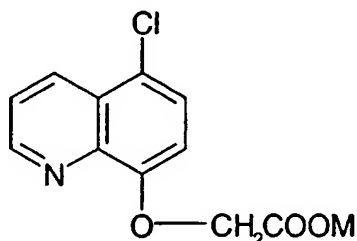
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safener (counter-agent, antidote) and which protects the useful plants, but not the weeds, against the phytotoxic action of the herbicide, as well as to the use of such a composition in the control of weeds in crops of useful plants.

There is accordingly also proposed according to the invention a selectively herbicidal composition which, in addition to comprising customary inert formulation adjuvants, such as carriers, solvents and wetting agents, comprises as active ingredient a mixture of

a) an amount, effective for herbicide synergy, of the compound of formula I and of one or more compounds selected from the compounds of formulae 2.1 to 2.7 and the compounds prosulfocarb, picolinafen, pyraflufen-ethyl, beflubutamid, fenoxaprop-P-ethyl, diclofop-methyl, amidosulfuron, flupyrsulfuron, flupyrsulfuron-methyl-sodium, metsulfuron-methyl, sulfosulfuron, tribenuron-methyl, imazamethabenz-methyl, flucarbazone, chlorotoluron, isoproturon, methabenzthiazuron, bifenox, fluoroglycofen-ethyl, imazosulfuron, diflufenican, bilanafos, ethalfluralin, trifluralin, fluthiamid, isoxaben, triallate, 2,4-DB, dichlorprop, MCPA, MCPB, mecoprop, MCPP, mecoprop-P, clopyralid, fluroxypyr, quinmerac, benazolin-ethyl, difenzoquat, cyhalofop-butyl, dithiopyr, quinclorac, prodiamine, benefin and trifluralin, and

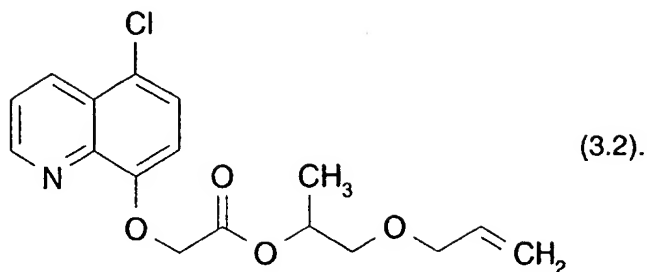
b) an amount, effective for herbicide antagonism, of a compound of formula 3.1



(3.1),

wherein M is a mono-, di- or tri-valent metal, ammonium, $N(R)_4$ or $HN(R)_3$, wherein the substituents R are identical or different and are C_1 - C_{16} alkyl or C_1 - C_{16} hydroxyalkyl, or M is $S(R_a)_3$ or $P(R_a)_4$, wherein the substituents R_a are identical or different and are C_1 - C_{20} alkyl, C_2 - C_{20} alkenyl, C_2 - C_{20} alkynyl, aryl substituted by C_1 - C_{20} alkyl, C_2 - C_{20} alkenyl or by C_2 - C_{20} alkynyl, or heteroaryl substituted by C_1 - C_{20} alkyl, C_2 - C_{20} alkenyl or by C_2 - C_{20} alkynyl, or two substituents R_a , together with the sulfur atom or phosphorus atom to which they are bonded, form a 5- or 6-membered ring, or the free acid thereof, or a hydrate of the 1-methylhexyl ester, especially 1-methylhexyl-(5-chloroquinolin-8-yloxy)acetate tetrahydrate, or of the compound of formula 3.2

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The invention relates also to a selectively herbicidal composition which, in addition to comprising customary inert formulation adjuvants, such as carriers, solvents and wetting agents, comprises as active ingredient a mixture of

- a) a herbicidally effective amount of the compound of formula I and
- b) an amount, effective for herbicide antagonism, of a compound of formula 3.1 or 3.2.

The metal atoms M which may be contained in formula 3.1 are preferably those of the alkali metal and alkaline earth metals, especially sodium, potassium, calcium, magnesium as well as, especially, aluminium and iron as preferred examples of trivalent metals.

Of the alkyl and hydroxyalkyl substituents R, preference is given to those having from 12 to 16 carbon atoms and also to those having from 1 to 4 carbon atoms. The groups $N(R)_4$ and $HN(R)_3$ contain especially a long-chain alkyl group as well as 2 or 3 short-chain alkyl groups, for example hexadecyl-triethylammonium, tetradecyl-triethylammonium, dodecyl-triethylammonium, dodecyl-ethyl-dimethylammonium and also tetradodecylammonium. Preferred alkyl groups R_a contain from 1 to 12, especially from 1 to 6, carbon atoms. The alkyl groups R and R_a may in turn be substituted, for example by halogen, alkoxy or haloalkoxy, preferably each having from 1 to 4 carbon atoms. Preferred alkenyl and alkynyl groups R_a contain from 2 to 12 carbon atoms. They may contain more than one unsaturated bond and may be substituted by halogen, alkoxy or haloalkoxy, preferably each having from 1 to 4 carbon atoms. Suitable examples of aryl groups R_a are phenyl, naphthyl, tetrahydronaphthyl, indanyl and indenyl, with phenyl being preferred. Those groups may be substituted by the above-mentioned alkyl, alkenyl and alkynyl groups. Heteroaryl groups R_a which may be mentioned are preferably 5- and 6-membered rings which contain especially nitrogen and/or oxygen atoms, for example pyridyl, pyrimidinyl, triazinyl, thienyl, thiazolyl, pyrazolyl, imidazolyl, piperidyl, dioxolanyl, morpholinyl and tetrahydrofuryl. These heterocycles may in turn also be substituted by the above-mentioned alkyl, alkenyl and alkynyl groups. Pairs of substituents R_a may form a ring together with the sulfur or phosphorus atom to which they are bonded. 5- or 6-membered saturated rings are preferably formed. The sulfonium and

phosphonium cations which can be used according to the invention are described, for example, in WO 00/44227.

In preferred compounds of formula 3.1, M is sodium, potassium or tri(hydroxyethylene)-ammonium.

In a further group of compounds of formula 3.1, M is calcium, magnesium, aluminium, iron, trimethylsulfonium, triphenylsulfonium, tetraphenylphosphonium, triphenyl-methyl-phosphonium, triphenyl-benzylphosphonium, C₁₂-C₁₆alkyl-trimethylammonium, C₁₂-C₁₆alkyl-triethylammonium, tetradodecylammonium or dodecyl-ethyl-dimethylammonium.

The salts of formula 3.1 can be prepared by customary methods, for example by reaction of the 2-(5-chloroquinolin-8-yloxy)-1-methylhexyl ester with an equimolar amount of a metal hydroxide in alcoholic solution at room temperature. The compound of formula 3.2 is described, for example, in US-A-6 162 762.

The salts listed in the following table are obtainable in that manner:

Table A: Compounds of formula 3.1:

Compound no.	M
2.01	Na
2.02	K
2.03	Ca
2.04	Mg
2.05	NH ₄
2.06	NH(CH ₂ CH ₂ OH) ₃
2.07	N(C ₁₂ H ₂₅) ₄
2.08	N(C ₁₂ H ₂₅)(C ₂ H ₅)(CH ₃) ₂
2.09	N(C ₁₂ H ₂₅)(CH ₃) ₃
2.10	N(C ₁₂ H ₂₅)(C ₂ H ₅) ₃
2.11	Al
2.12	Fe

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Compound no.	M
2.13	H
2.14	$S(CH_3)_3$
2.15	$S(C_6H_5)_3$
2.16	$P(C_6H_5)_4$
2.17	$P(C_6H_5)_3CH_3$
2.18	$P(C_6H_5)_3CH_2C_6H_5$

Further preferred compositions according to the invention comprise a compound of formula 2.6 and an amount, effective for herbicide antagonism, of the compound of formula 3.1 or the free acid thereof or of a hydrate of the 1-methylhexyl ester.

The invention relates also to a method for the selective control of weeds in crops of useful plants, which comprises treating the useful plants, seeds or cuttings thereof, or the area of cultivation thereof, with a herbicidally effective amount of the herbicide of formula I, optionally one or more herbicides selected from the compounds of formulae 2.1 to 2.7 and the compounds prosulfocarb, picolinafen, pyraflufen-ethyl, beflubutamid, fenoxaprop-P-ethyl, diclofop-methyl, amidosulfuron, flupyrsulfuron, flupyrsulfuron-methyl-sodium, metsulfuron-methyl, sulfosulfuron, tribenuron-methyl, imazamethabenz-methyl, flucarbazone, chlorotoluron, isoproturon, methabenzthiazuron, bifenox, fluoroglycofen-ethyl, imazosulfuron, diflufenican, bilanafos, ethalfluralin, trifluralin, fluthiamid, isoxaben, triallate, 2,4-DB, dichlorprop, MCPA, MCPB, mecoprop, MCPP, mecoprop-P, clopyralid, fluroxypyr, quinmerac, benazolin-ethyl, difenzoquat, cyhalofop-butyl, dithiopyr, quinclorac, prodiamine, benefin and trifluralin, and an amount, effective for herbicide antagonism, of a safener of formula 3.1 or 3.2.

As crop plants that can be protected by the safeners of formula 3.1 or 3.2 against the damaging effect of the above-mentioned herbicides there come into consideration especially cereals, cotton, soybeans, sugar beet, sugar cane, plantation crops, rape, maize and rice, very especially cereals. "Crops" are to be understood to mean also those crops which have been made tolerant to herbicides or classes of herbicides as a result of conventional methods of breeding or genetic engineering.

The weeds to be controlled may be both monocotyledonous and dicotyledonous weeds, for example *Stellaria*, *Agrostis*, *Digitaria*, *Avena*, *Apera*, *Brachiaria*, *Phalaris*, *Setaria*, *Sinapis*, *Lolium*, *Solanum*, *Echinochloa*, *Scirpus*, *Monochoria*, *Sagittaria*, *Panicum*, *Bromus*, *Alopecurus*, *Sorghum halepense*, *Sorghum bicolor*, *Rottboellia*, *Cyperus*, *Abutilon*, *Sida*, *Xanthium*, *Amaranthus*, *Chenopodium*, *Ipomoea*, *Chrysanthemum*, *Galium*, *Viola* and *Veronica*.

Areas of cultivation include the areas of ground on which the crop plants are already growing or which have already been sown with the seeds of those crop plants, as well as ground intended for cultivation with such crop plants.

Depending on the intended use, a safener of formula 3.1 or 3.2 can be used to pretreat the seed of the crop plant (dressing of the seeds or cuttings) or can be introduced into the soil before or after sowing. It can, however, also be applied alone or together with the herbicide after emergence of the plants. The treatment of the plants or seeds with the safener can therefore in principle be carried out independently of the time at which the herbicide is applied. The plants can, however, also be treated by simultaneous application of herbicide and safener (e.g. in the form of a tank mixture). The ratio of the rate of application of safener to the rate of application of herbicide depends largely on the method of application. In the case of field treatment, which is carried out either using a tank mixture comprising a combination of safener and herbicide or by separate application of safener and herbicide, the ratio of herbicides to safener is generally from 100:1 to 1:10, preferably from 20:1 to 1:1. In the case of field treatment it is usual to apply from 0.001 to 1.0 kg of safener/ha, preferably from 0.001 to 0.25 kg of safener/ha.

The rate of application of herbicides is generally from 0.001 to 0.5 kg/ha, but preferably from 0.005 to 0.5 kg/ha.

The compositions according to the invention are suitable for all methods of application conventionally used in agriculture, for example pre-emergence application, post-emergence application and seed dressing.

In the case of seed dressing, generally from 0.001 to 10 g of safener/kg of seed, preferably from 0.05 to 2 g of safener/kg of seed, are applied. When the safener is applied in liquid

form shortly before sowing, with soaking of the seeds, then there are advantageously used safener solutions that comprise the active ingredient in a concentration of from 1 to 10 000 ppm, preferably from 100 to 1000 ppm.

For the purpose of application, the safeners of formula 3.1 or 3.2 or combinations of those safeners with the herbicide of formula I and, optionally, one or more herbicides selected from the compounds of formulae 2.1 to 2.7 and the compounds prosulfocarb, picolinafen, pyraflufen-ethyl, beflubutamid, fenoxaprop-P-ethyl, diclofop-methyl, amidosulfuron, flupyrsulfuron, flupyrsulfuron-methyl-sodium, metsulfuron-methyl, sulfosulfuron, tribenuron-methyl, imazamethabenz-methyl, flucarbazone, chlorotoluron, isoproturon, methabenzthiazuron, bifenox, fluoroglycofen-ethyl, imazosulfuron, diflufenican, bilanafos, ethalfluralin, trifluralin, fluthiamid, isoxaben, triallate, 2,4-DB, dichlorprop, MCPA, MCPB, mecoprop, MCPP, mecoprop-P, clopyralid, fluroxypyr, quinmerac, benazolin-ethyl, difenzoquat, cyhalofop-butyl, dithiopyr, quinclorac, prodiamine, benefin and trifluralin are advantageously formulated together with the adjuvants conventionally employed in formulation technology, e.g. into emulsifiable concentrates, coatable pastes, directly sprayable or dilutable solutions, dilute emulsions, wettable powders, soluble powders, dusts, granules or microcapsules.

Such formulations are described, for example, on pages 9 to 13 of WO 97/34485. The formulations are prepared in known manner, e.g. by intimately mixing and/or grinding the active ingredients with liquid or solid formulation adjuvants, e.g. solvents or solid carriers. Surface-active compounds (surfactants) can additionally also be used in the preparation of the formulations. Solvents and solid carriers suitable for that purpose are mentioned, for example, on page 6 of WO 97/34485.

Depending on the identity of the compounds of formulae I, 2.1 to 2.7 and prosulfocarb, picolinafen, pyraflufen-ethyl, beflubutamid, fenoxaprop-P-ethyl, diclofop-methyl, amidosulfuron, flupyrsulfuron, flupyrsulfuron-methyl-sodium, metsulfuron-methyl, sulfosulfuron, tribenuron-methyl, imazamethabenz-methyl, flucarbazone, chlorotoluron, isoproturon, methabenzthiazuron, bifenox, fluoroglycofen-ethyl, imazosulfuron, diflufenican, bilanafos, ethalfluralin, trifluralin, fluthiamid, isoxaben, triallate, 2,4-DB, dichlorprop, MCPA, MCPB, mecoprop, MCPP, mecoprop-P, clopyralid, fluroxypyr, quinmerac, benazolin-ethyl, difenzoquat, cyhalofop-butyl, dithiopyr, quinclorac, prodiamine, benefin and trifluralin and 3.1 and 3.2 to be formulated, suitable surface-active compounds are non-ionic, cationic and/or

anionic surfactants and surfactant mixtures having good emulsifying, dispersing and wetting properties. Examples of suitable anionic, non-ionic and cationic surfactants are listed, for example, on pages 7 and 8 of WO 97/34485. Also suitable for the preparation of the herbicidal compositions according to the invention are the surfactants conventionally employed in formulation technology, which are described, *inter alia*, in "McCutcheon's Detergents and Emulsifiers Annual" MC Publishing Corp., Ridgewood New Jersey, 1981, Stache, H., "Tensid-Taschenbuch", Carl Hanser Verlag, Munich/Vienna, 1981 and M. and J. Ash, "Encyclopedia of Surfactants", Vol. I-III, Chemical Publishing Co., New York, 1980-81.

The herbicidal formulations usually comprise from 0.1 to 99 % by weight, especially from 0.1 to 95 % by weight, of active ingredient mixture comprising the compound of formula I, a compound selected from the compounds of formulae 2.1 to 2.7 and the compounds prosulfocarb, picolinafen, pyraflufen-ethyl, beflubutamid, fenoxaprop-P-ethyl, diclofop-methyl, amidosulfuron, flupyrsulfuron, flupyrsulfuron-methyl-sodium, metsulfuron-methyl, sulfosulfuron, tribenuron-methyl, imazamethabenz-methyl, flucarbazone, chlorotoluron, isoproturon, methabenzthiazuron, bifenoxy, fluoroglycofen-ethyl, imazosulfuron, diflufenican, bilanafos, ethalfluralin, trifluralin, fluthiamid, isoxaben, triallate, 2,4-DB, dichlorprop, MCPA, MCPB, mecoprop, MCPP, mecoprop-P, clopyralid, fluroxypyr, quinmerac, benazolin-ethyl, difenzoquat, cyhalofop-butyl, dithiopyr, quinclorac, prodiamine, benefin and trifluralin, and the compounds of formula 3.1 or 3.2, from 1 to 99.9 % by weight of a solid or liquid formulation adjuvant and from 0 to 25 % by weight, especially from 0.1 to 25 % by weight, of a surfactant. Whereas commercial products will preferably be formulated as concentrates, the end user will normally employ dilute formulations.

The compositions may also comprise further additives, such as stabilisers, for example vegetable oils or epoxidised vegetable oils (epoxidised coconut oil, rapeseed oil or soybean oil), anti-foams, e.g. silicone oil, preservatives, viscosity regulators, binders, tackifiers, and also fertilisers or other active ingredients. For the use of safeners of formula 3.1 or 3.2, or of compositions comprising them, in the protection of crop plants against the damaging effects of herbicides of formulae I and 2.1 to 2.7 and the compounds prosulfocarb, picolinafen, pyraflufen-ethyl, beflubutamid, fenoxaprop-P-ethyl, diclofop-methyl, amidosulfuron, flupyrsulfuron, flupyrsulfuron-methyl-sodium, metsulfuron-methyl, sulfosulfuron, tribenuron-methyl, imazamethabenz-methyl, flucarbazone, chlorotoluron, isoproturon, methabenz-

thiazuron, bifenox, fluoroglycofen-ethyl, imazosulfuron, diflufenican, bilanafos, ethalfluralin, trifluralin, fluthiamid, isoxaben, triallate, 2,4-DB, dichlorprop, MCPA, MCPB, mecoprop, MCPP, mecoprop-P, clopyralid, fluroxypyr, quinmerac, benazolin-ethyl, difenzoquat, cyhalofop-butyl, dithiopyr, quinclorac, prodiamine, benefin and trifluralin, various methods and techniques come into consideration, such as, for example, the following:

i) Seed dressing

- a) Dressing of the seeds with a wettable powder formulation of the compound of formula 3.1 or 3.2 by shaking in a vessel until uniformly distributed over the seed surface (dry dressing). In that procedure approximately from 1 to 500 g of compound of formula 3.1 or 3.2 (4 g to 2 kg of wettable powder) are used per 100 kg of seed.
- b) Dressing of the seeds with an emulsifiable concentrate of the compound of formula 3.1 according to method a) (wet dressing).
- c) Dressing by immersing the seeds for from 1 to 72 hours in a liquor comprising from 100 to 1000 ppm of the compound of formula 3.1 or 3.2 and optionally subsequently drying the seeds (immersion dressing).

Dressing the seed or treating the germinated seedling are naturally the preferred methods of application, because treatment with the active ingredients is directed entirely at the target crop. Generally from 1 to 1000 g of antidote, preferably from 5 to 250 g of antidote, are used per 100 kg of seed, but depending on the methodology, which also allows other active ingredients or micronutrients to be added, concentrations above or below the limits indicated may be employed (repeat dressing).

ii) Application as a tank mixture

A liquid formulation of a mixture of antidote and herbicide is used (ratio by weight of the one to the other from 10:1 to 1:100), the rate of application of herbicide being from 0.005 to 5.0 kg per hectare. Such tank mixtures are applied before or after sowing.

iii) Application to the seed furrow

The compound of formula 3.1 or 3.2 is introduced into the open, sown seed furrow in the form of an emulsifiable concentrate, wettable powder or granules. Once the seed furrow has been covered over, the herbicide is applied in the usual manner pre-emergence.

iv) Controlled release of active ingredient

The compound of formula 3.1 or 3.2 is applied in solution to mineral granule carriers or polymerised granules (urea/formaldehyde) and dried. If desired, it is also possible to apply a coating that allows the active ingredient to be released in metered amounts over a specific period of time (coated granules).

Preferred formulations have especially the following compositions:

(% = percent by weight)

Emulsifiable concentrates:

active ingredient mixture:	1 to 90 %, preferably 5 to 20 %
surfactant:	1 to 30 %, preferably 10 to 20 %
liquid carrier:	5 to 94 %, preferably 70 to 85 %

Dusts:

active ingredient mixture:	0.1 to 10 %, preferably 0.1 to 5 %
solid carrier:	99.9 to 90 %, preferably 99.9 to 99 %

Suspension concentrates:

active ingredient mixture:	5 to 75 %, preferably 10 to 50 %
water:	94 to 24 %, preferably 88 to 30 %
surfactant:	1 to 40 %, preferably 2 to 30 %

Wettable powders:

active ingredient mixture:	0.5 to 90 %, preferably 1 to 80 %
surfactant:	0.5 to 20 %, preferably 1 to 15 %
solid carrier:	5 to 95 %, preferably 15 to 90 %

Granules:

active ingredient mixture:	0.1 to 30 %, preferably 0.1 to 15 %
solid carrier:	99.5 to 70 %, preferably 97 to 85 %

The following Examples further illustrate but do not limit the invention.

Formulation Examples for mixtures of herbicides of formula I and optionally of formulae 2.1 to 2.7 and the compounds prosulfocarb, picolinafen, pyraflufen-ethyl, beflubutamid, fenoxaprop-P-ethyl, diclofop-methyl, amidosulfuron, flupyrsulfuron, flupyrsulfuron-methyl-sodium, metsulfuron-methyl, sulfosulfuron, tribenuron-methyl, imazamethabenz-methyl, flucarbazone, chlorotoluron, isoproturon, methabenzthiazuron, bifenox, fluoroglycofen-ethyl, imazosulfuron, diflufenican, bilanafos, ethalfluralin, trifluralin, fluthiamid, isoxaben, triallate, 2,4-DB, dichlorprop, MCPA, MCPB, mecoprop, MCPP, mecoprop-P, clopyralid, fluroxypyr, quinmerac, benazolin-ethyl, difenzoquat, cyhalofop-butyl, dithiopyr, quinclorac, prodiamine, benefin and trifluralin, and safeners of formula 3.1 or 3.2 (% = percent by weight)

<u>F1. Emulsifiable concentrates</u>	a)	b)	c)	d)
active ingredient mixture	5 %	10 %	25 %	50 %
calcium dodecylbenzenesulfonate	6 %	8 %	6 %	8 %
castor oil polyglycol ether	4 %	-	4 %	4 %
(36 mol of ethylene oxide)				
octylphenol polyglycol ether	-	4 %	-	2 %
(7-8 mol of ethylene oxide)				
cyclohexanone	-	-	10 %	20 %
arom. hydrocarbon mixture	85 %	78 %	55 %	16 %

C₉-C₁₂

Emulsions of any desired concentration can be obtained from such concentrates by dilution with water.

<u>F2. Solutions</u>	a)	b)	c)	d)
active ingredient mixture	5 %	10 %	50 %	90 %
1-methoxy-3-(3-methoxy-propoxy)-propane	-	20 %	20 %	-
polyethylene glycol MW 400	20 %	10 %	-	-
N-methyl-2-pyrrolidone	-	-	30 %	10 %
arom. hydrocarbon mixture	75 %	60 %	-	-

C₉-C₁₂

The solutions are suitable for use in the form of microdrops.

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<u>F3. Wettable powders</u>	a)	b)	c)	d)
active ingredient mixture	5 %	25 %	50 %	80 %
sodium lignosulfonate	4 %	-	3 %	-
sodium lauryl sulfate	2 %	3 %	-	4 %
sodium diisobutyl naphthalene-sulfonate	-	6 %	5 %	6 %
octylphenol polyglycol ether (7-8 mol of ethylene oxide)	-	1 %	2 %	-
highly dispersed silicic acid	1 %	3 %	5 %	10 %
kaolin	88 %	62 %	35 %	-

The active ingredient is mixed thoroughly with the adjuvants and the mixture is thoroughly ground in a suitable mill, affording wettable powders which can be diluted with water to give suspensions of any desired concentration.

<u>F4. Coated granules</u>	a)	b)	c)
active ingredient mixture	0.1 %	5 %	15 %
highly dispersed silicic acid	0.9 %	2 %	2 %
inorganic carrier	99.0 %	93 %	83 %

(diameter 0.1 - 1 mm)

e.g. CaCO_3 or SiO_2

The active ingredient is dissolved in methylene chloride and applied to the carrier by spraying, and the solvent is then evaporated off *in vacuo*.

<u>F5. Coated granules</u>	a)	b)	c)
active ingredient mixture	0.1 %	5 %	15 %
polyethylene glycol MW 200	1.0 %	2 %	3 %
highly dispersed silicic acid	0.9 %	1 %	2 %
inorganic carrier	98.0 %	92 %	80 %

(diameter 0.1 - 1 mm)

e.g. CaCO_3 or SiO_2

The finely ground active ingredient is uniformly applied, in a mixer, to the carrier moistened with polyethylene glycol. Non-dusty coated granules are obtained in this manner.

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<u>F6. Extruder granules</u>	a)	b)	c)	d)
active ingredient mixture	0.1 %	3 %	5 %	15 %
sodium lignosulfonate	1.5 %	2 %	3 %	4 %
carboxymethylcellulose	1.4 %	2 %	2 %	2 %
kaolin	97.0 %	93 %	90 %	79 %

The active ingredient is mixed and ground with the adjuvants, and the mixture is moistened with water. The mixture is extruded and then dried in a stream of air.

<u>F7. Dusts</u>	a)	b)	c)
active ingredient mixture	0.1 %	1 %	5 %
talcum	39.9 %	49 %	35 %
kaolin	60.0 %	50 %	60 %

Ready-to-use dusts are obtained by mixing the active ingredient with the carriers and grinding the mixture in a suitable mill.

<u>F8. Suspension concentrates</u>	a)	b)	c)	d)
active ingredient mixture	3 %	10 %	25 %	50 %
ethylene glycol	5 %	5 %	5 %	5 %
nonylphenol polyglycol ether (15 mol of ethylene oxide)	-	1 %	2 %	-
sodium lignosulfonate	3 %	3 %	4 %	5 %
carboxymethylcellulose	1 %	1 %	1 %	1 %
37 % aqueous formaldehyde solution	0.2 %	0.2 %	0.2 %	0.2 %
silicone oil emulsion	0.8 %	0.8 %	0.8 %	0.8 %
water	87 %	79 %	62 %	38 %

The finely ground active ingredient is intimately mixed with the adjuvants, giving a suspension concentrate from which suspensions of any desired concentration can be obtained by dilution with water.

It is often more practical for the active ingredients of formulae I, 2.1 to 2.7 and prosulfocarb, picolinafen, pyraflufen-ethyl, beflubutamid, fenoxaprop-P-ethyl, diclofop-methyl, amidosulfuron, flupyrsulfuron, flupyrsulfuron-methyl-sodium, metsulfuron-methyl, sulfosulfuron, tribenuron-methyl, imazamethabenz-methyl, flucarbazone, chlorotoluron,

isoproturon, methabenzthiazuron, bifenox, fluoroglycofen-ethyl, imazosulfuron, diflufenican, bilanafos, ethalfluralin, trifluralin, fluthiamid, isoxaben, triallate, 2,4-DB, dichlorprop, MCPA, MCPB, mecoprop, MCPP, mecoprop-P, clopyralid, fluroxypyr, quinmerac, benazolin-ethyl, difenzoquat, cyhalofop-butyl, dithiopyr, quinclorac, prodiamine, benefin and trifluralin, and 3.1 and 3.2 to be formulated separately and then to be brought together in the desired mixing ratio in the applicator in the form of a "tank mixture" in water shortly before application.

The ability of the safeners of formula 3.1 or 3.2 to protect crop plants against the phytotoxic action of herbicides of formula I is illustrated in the following Example.

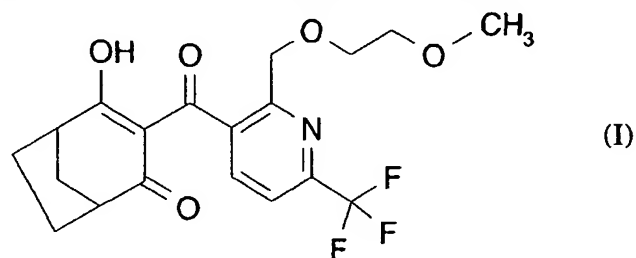
Biological Example: safening action

The test plants are grown in plastics pots under greenhouse conditions to the 4-leaf stage. At that stage, the herbicides alone and the mixtures of the herbicides with the test compounds to be tested as safeners are applied to the test plants. The test compounds are applied in the form of an aqueous suspension prepared from a 25 % wettable powder (Example F3, b)) or from a suspension concentrate as in Example F8, with 500 litres of water/ha. 3 weeks after application, the phytotoxic action of the herbicides on the crop plants, e.g. maize and cereals, is evaluated using a percentage scale. 100 % indicates that the test plant has died, 0 % indicates no phytotoxic action. The mixtures according to the invention exhibit good action in this test.

What is claimed is:

1. A selectively herbicidal composition which, in addition to comprising customary inert formulation adjuvants, comprises as active ingredient a mixture of

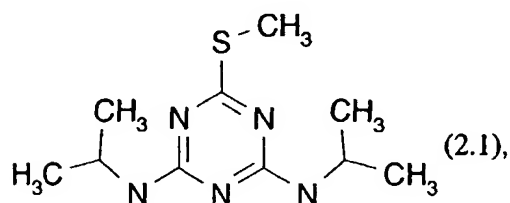
a) a herbicidally effective amount of the compound of formula I



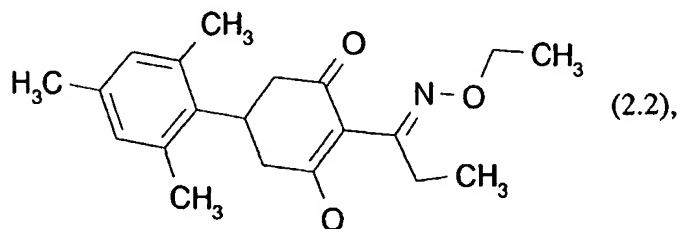
or of an agronomically tolerable salt of that compound, and

b) a synergistically effective amount of one or more compounds selected from

the compound of formula 2.1

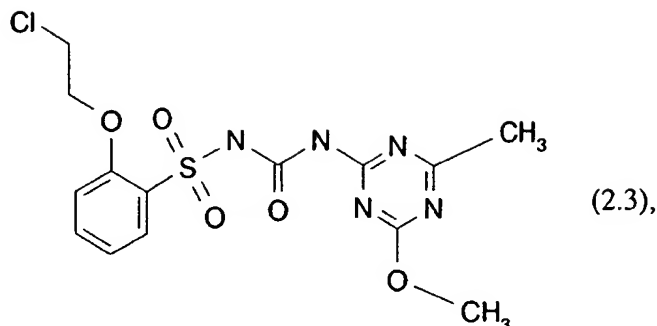


and the compound of formula 2.2

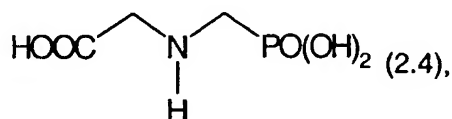


and the compound of formula 2.3

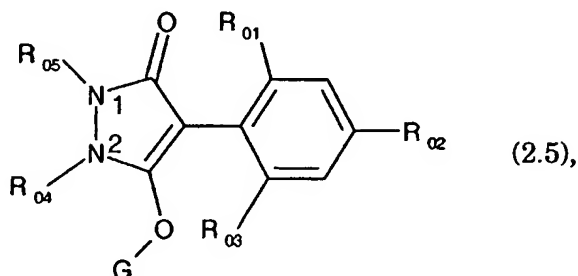
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and the ammonium, isopropylammonium, sodium and trimesium salts of the compound of formula 2.4



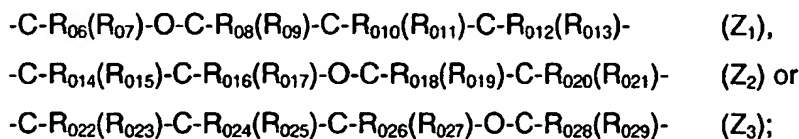
and a compound of formula 2.5



wherein

R_{01} , R_{02} and R_{03} are each independently of the others halogen, nitro, cyano, C_1 - C_4 alkyl, C_2 - C_4 alkenyl, C_2 - C_4 alkynyl, C_1 - C_4 haloalkyl, C_2 - C_6 haloalkenyl, C_3 - C_6 cycloalkyl, halo-substituted C_3 - C_6 cycloalkyl, C_1 - C_6 alkoxyalkyl, C_1 - C_6 alkylthioalkyl, hydroxy, mercapto, C_1 - C_6 alkoxy, C_3 - C_6 alkenyloxy, C_3 - C_6 alkynyloxy, C_1 - C_4 alkylcarbonyl, C_1 - C_4 alkoxycarbonyl, C_1 - C_4 alkylthio, C_1 - C_4 alkylsulfinyl, C_1 - C_4 alkylsulfonyl, amino, C_1 - C_4 alkylamino or di(C_1 - C_4 alkyl)-amino;

R_{04} and R_{05} together are a group



wherein R_{06} , R_{07} , R_{08} , R_{09} , R_{010} , R_{011} , R_{012} , R_{013} , R_{014} , R_{015} , R_{016} , R_{017} , R_{018} , R_{019} , R_{020} , R_{021} , R_{022} , R_{023} , R_{024} , R_{025} , R_{026} , R_{027} , R_{028} and R_{029} are each independently of the others hydrogen,

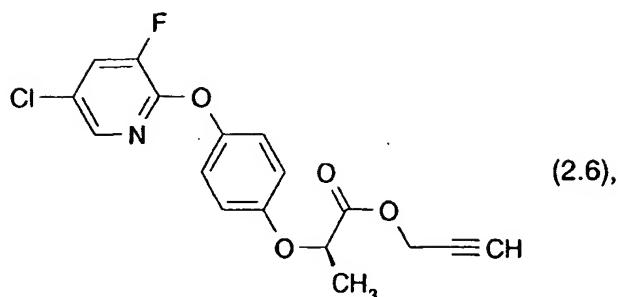
halogen, C₁-C₄alkyl or C₁-C₄haloalkyl, wherein there may be either fused or spiro-bound to the carbon atoms of groups Z₁, Z₂ or Z₃ an alkylene ring which together with the carbon atoms of groups Z₁, Z₂ or Z₃ contains from 2 to 6 carbon atoms and which may be interrupted by oxygen, or that alkylene ring bridges at least one ring atom of the groups Z₁, Z₂ or Z₃; G is hydrogen, -C(X₁)-R₀₃₀, -C(X₂)-X₃-R₀₃₁, -C(X₄)-N(R₀₃₂)-R₀₃₃, -SO₂-R₀₃₄, an alkali metal, alkaline earth metal, sulfonium or ammonium cation, or -P(X₅)(R₀₃₅)-R₀₃₆;

X₁, X₂, X₃, X₄ and X₅ are each independently of the others oxygen or sulfur; and

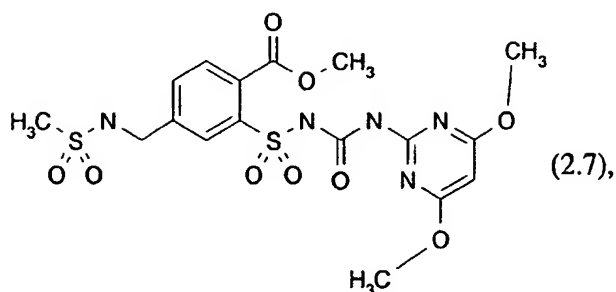
R₀₃₀, R₀₃₁, R₀₃₂, R₀₃₃, R₀₃₄, R₀₃₅ and R₀₃₆ are each independently of the others hydrogen, C₁-C₅alkyl, C₁-C₅haloalkyl, C₂-C₅alkenyl, C₁-C₅alkoxyalkyl, C₃-C₆cycloalkyl or phenyl, and R₀₃₄ may additionally be C₂-C₂₀alkenyl, C₂-C₂₀alkenyl substituted by halogen, alkylcarbonyl, alkoxycarbonyl, alkylcarbonyloxy, alkoxy, thioalkyl, alkylthiocarbonyl, alkylcarbonylthio, alkylsulfonyl, alkylsulfoxyl, alkylaminosulfonyl, dialkylaminosulfonyl, alkylsulfonyloxy, alkylsulfonylamino, alkylamino, dialkylamino, alkylcarbonylamino, dialkylcarbonylamino, alkyl-alkylcarbonylamino, cyano, (C₃-C₇)cycloalkyl, (C₃-C₇)heterocyclyl, trialkylsilyl, trialkylsilyloxy, phenyl, substituted phenyl, heteroaryl or by substituted heteroaryl, C₂-C₂₀alkynyl, C₂-C₂₀alkynyl substituted by halogen, alkylcarbonyl, alkoxycarbonyl, alkylcarbonyloxy, alkoxy, thioalkyl, alkylthiocarbonyl, alkylcarbonylthio, alkylsulfonyl, alkylsulfoxyl, alkylaminosulfonyl, dialkylaminosulfonyl, alkylsulfonyloxy, alkylsulfonylamino, alkylamino, dialkylamino, alkylcarbonylamino, dialkylcarbonylamino, alkyl-alkylcarbonylamino, cyano, (C₃-C₇)cycloalkyl, (C₃-C₇)heterocyclyl, trialkylsilyl, trialkylsilyloxy, phenyl, substituted phenyl, heteroaryl or by substituted heteroaryl, (C₁-C₇)cycloalkyl, (C₁-C₇)cycloalkyl substituted by halogen, haloalkyl, (C₁-C₆)alkyl, alkoxy, alkylcarbonyloxy, thioalkyl, alkylcarbonylthio, alkylamino, alkylcarbonylamino, trialkylsilyl or by trialkylsilyloxy, heteroaryl, heteroaryl substituted by halogen, haloalkyl, nitro, cyano, (C₁-C₆)alkyl, alkoxy, alkylcarbonyloxy, thioalkyl, alkylcarbonylthio, alkylamino, alkylcarbonylamino, trialkylsilyl or by trialkylsilyloxy, heteroaryloxy, substituted heteroaryloxy, heteroarylthio, substituted heteroarylthio, heteroarylamino, substituted heteroarylamino, diheteroarylamino, substituted diheteroarylamino, phenylamino, substituted phenylamino, diphenylamino, substituted diphenylamino, cycloalkylamino, substituted cycloalkylamino, dicycloalkylamino, substituted dicycloalkylamino, cycloalkoxy or substituted cycloalkoxy, and also salts and diastereoisomers of the compounds of formula 2.5,

and the compound of formula 2.6

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and the compound of formula 2.7



and the compounds prosulfocarb, picolinafen, pyraflufen-ethyl, beflubutamid, fenoxaprop-P-ethyl, diclofop-methyl, amidosulfuron, flupyrsulfuron, flupyrsulfuron-methyl-sodium, metsulfuron-methyl, sulfosulfuron, tribenuron-methyl, imazamethabenz-methyl, flucarbazone, chlorotoluron, isoproturon, methabenzthiazuron, bifenox, fluoroglycofen-ethyl, imazosulfuron, diflufenican, bilanafos, ethalfluralin, trifluralin, fluthiamid, isoxaben, triallate, 2,4-DB, dichlorprop, MCPA, MCPB, mecoprop, MCPP, mecoprop-P, clopyralid, fluroxypyr, quinmerac, benazolin-ethyl, difenzoquat, cyhalofop-butyl, dithiopyr, quinclorac, prodiamine, benefin and trifluralin.

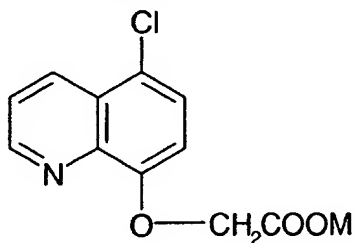
2. A method of controlling undesired plant growth in crops of useful plants, which comprises allowing a herbicidally effective amount of a composition according to claim 1 to act on the cultivated plant or its locus.

3. A method according to claim 2, wherein the cultivated plant is maize or a cereal.

4. A method according to claim 2, wherein the useful plant crop is treated with the mentioned composition at rates of application corresponding to a total amount of from 1 to 5000 g of active ingredient per hectare.

5. A selectively herbicidal composition which, in addition to comprising customary inert formulation adjuvants, such as carriers, solvents and wetting agents, comprises as active ingredient a mixture of

- a) an amount, effective for herbicide synergy, of the compound of formula I according to claim 1 and of one or more compounds selected from the compounds of formulae 2.1 to 2.7 according to claim 1 and the compounds prosulfocarb, picolinafen, pyraflufen-ethyl, beflubutamid, fenoxaprop-P-ethyl, diclofop-methyl, amidosulfuron, flupyrsulfuron, flupyrsulfuron-methyl-sodium, metsulfuron-methyl, sulfosulfuron, tribenuron-methyl, imazamethabenz-methyl, flucarbazone, chlorotoluron, isoproturon, methabenzthiazuron, bifenox, fluoroglycofen-ethyl, imazosulfuron, diflufenican, bilanafos, ethalfluralin, trifluralin, fluthiamid, isoxaben, triallate, 2,4-DB, dichlorprop, MCPA, MCPB, mecoprop, MCPP, mecoprop-P, clopyralid, fluroxypyr, quinmerac, benazolin-ethyl, difenzoquat, cyhalofop-butyl, dithiopyr, quinclorac, prodiamine, benefin and trifluralin, and
- b) an amount, effective for herbicide antagonism, of a compound of formula 3.1

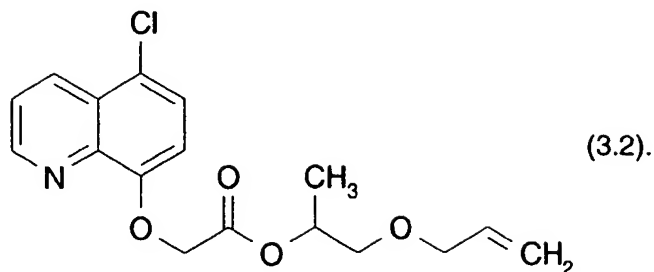


(3.1),

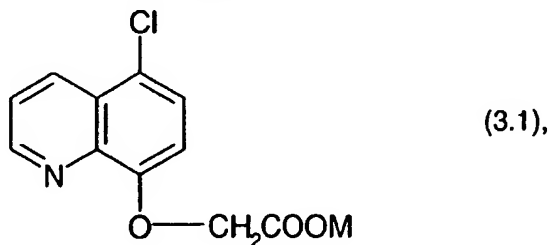
wherein M is a mono-, di- or tri-valent metal, ammonium, $N(R)_4$ or $HN(R)_3$, wherein the substituents R are identical or different and are C_1 - C_{16} alkyl or C_1 - C_{16} hydroxyalkyl, or M is $S(R_a)_3$ or $P(R_a)_4$, wherein the substituents R_a are identical or different and are C_1 - C_{20} alkyl, C_2 - C_{20} alkenyl, C_2 - C_{20} alkynyl, aryl substituted by C_1 - C_{20} alkyl, C_2 - C_{20} alkenyl or by C_2 - C_{20} alkynyl, or heteroaryl substituted by C_1 - C_{20} alkyl, C_2 - C_{20} alkenyl or by C_2 - C_{20} alkynyl, or two substituents R_a , together with the sulfur atom or phosphorus atom to which they are bonded, form a 5- or 6-membered ring, or the free acid thereof, or a hydrate of the 1-methylhexyl ester,

or of formula 3.2

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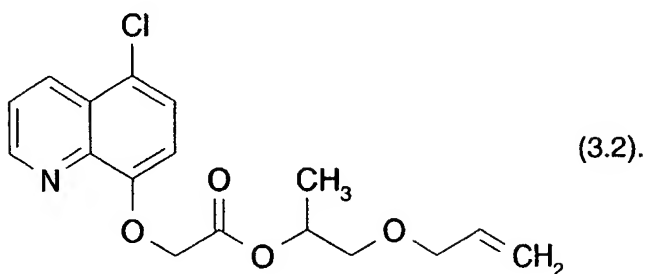
6. A method of selectively controlling weeds and grasses in crops of useful plants, which comprises treating the useful plants, seeds or cuttings thereof or the area of cultivation thereof with an amount, effective for herbicide synergy, of a composition according to claim 5.
7. A method according to claim 6, wherein the rate of application of herbicides is from 1 to 5000 g/ha and the rate of application of safener is from 0.001 to 0.5 kg/ha.
8. A method according to claim 6, wherein the useful plant crop is maize or a cereal.
9. A selectively herbicidal composition which, in addition to comprising customary inert formulation adjuvants, such as carriers, solvents and wetting agents, comprises as active ingredient a mixture of
- a herbicidally effective amount of the compound of formula I according to claim 1, and
 - an amount, effective for herbicide antagonism, of the compound of formula 3.1



wherein M is a mono-, di- or tri-valent metal, ammonium, $N(R)_4$ or $HN(R)_3$, wherein the substituents R are identical or different and are C_1 - C_{16} alkyl or C_1 - C_{16} hydroxyalkyl, or M is $S(R_a)_3$ or $P(R_a)_4$, wherein the substituents R_a are identical or different and are C_1 - C_{20} alkyl, C_2 - C_{20} alkenyl, C_2 - C_{20} alkynyl, aryl substituted by C_1 - C_{20} alkyl, C_2 - C_{20} alkenyl or by C_2 - C_{20} alkynyl, or heteroaryl substituted by C_1 - C_{20} alkyl, C_2 - C_{20} alkenyl or by C_2 - C_{20} alkynyl, or two substituents R_a , together with the sulfur atom or phosphorus atom to which they are bonded,

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form a 5- or 6-membered ring, or the free acid thereof, or a hydrate of the 1-methylhexyl ester,
or of formula 3.2



10. A method of selectively controlling weeds and grasses in crops of useful plants, which comprises treating the useful plants, seeds or cuttings thereof or the area of cultivation thereof with a selectively herbicidal amount of a composition according to claim 9.

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